

Freeze-thaw controlled aggregation mechanism of humic acid-coated goethite: Implications for organic carbon preservation

HPSTAR
1358-2022

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ARTICLE INFO

Handling Editor: Cornelia Rumpel

Keywords:

Goethite
Humic acid
Aggregates
Freeze–thaw
Ice exclusion
Carbon

ABSTRACT

Organic carbon sequestered in soil aggregate contributes significantly to the carbon preservation on the earth's surface. However, the turnover of soil aggregate in high latitudes and cold zones is strongly affected by the frequency of freeze–thaw cycles and may be disturbed by climate change. Although the effects of recurrent freeze–thaw cycles on the size, structure, and stability of soil aggregate have been well studied, the aggregation of individual mineral particles adsorbed by organic carbon and its mechanism are not yet conclusive. Here, we report that more than 97 wt% of the humic acid-coated goethite (goethite-HA) particles can aggregate into aggregates of different sizes and morphologies through one freeze–thaw cycle (freezing at $-24\text{ }^{\circ}\text{C}$ for 12 h and thawing at $4\text{ }^{\circ}\text{C}$ for 12 h). Combining electron microscopy, infrared absorption spectroscopy and thermogravimetric analysis, we revealed that goethite-HA particles could strongly complex with each other after one freeze–thaw cycle. Compared with previous studies, our results showed that both electrostatic repulsion and steric hindrance (known to prevent aggregation) were overcome by the internal thrust of ice exclusion during freezing, then goethite-HA particles could be interconnected through the carboxyl-iron and hydrogen bonding to form aggregates. We believe that aggregates formed during the freeze–thaw cycles in soils rich in iron (hydr) oxides can serve as shelters for soil organic carbon and may reduce CO_2 emissions in these soils.

1. Introduction

The soil process involves the largest amount of active carbon of the earth's surface, which is greater than that of the atmosphere and the vegetation combined (Lal, 2004). Many soil processes are carried out in the unit of soil aggregate. Chemically, soil aggregates are primarily made from soil mineral particles and binding agents. Compared with free-standing soil mineral particles, mineral particles in soil aggregate have much stronger physicochemical interactions with each other (Bronick and Lal, 2005; Tisdall and Oades, 1982) and construct a larger volume for holding and preserving more organic carbons. Soil aggregates not only mediate the chemical, physical and biological processes of soil, but also play a vital role in the preservation of organic carbon due to their inherent physical separation (Goebel et al., 2005; Yudina and Kuzakov, 2019). Therefore, the stability of soil aggregates is critical for tuning the carbon budget in the biosphere and may help alleviate soil

carbon emissions into the atmosphere. Pioneering research had shown several factors may affect the stability of soil aggregate, such as parent mineral particles, planting system, soil organic matter, and general climate change (Guan et al., 2018; Harris et al., 1966; Jastrow, 1996; Yang et al., 2019; Zhao et al., 2017). Among them, global climate change has witnessed a tremendous change in the global carbon level in the last decade and may dramatically influence the so-called freeze–thaw cycles (FTCs), which often occur in cold winter zones. The frequency and intensity of FTCs are mainly controlled by local climatic conditions (Yu et al., 2011). For example, up to 55% of the total land in the northern hemisphere was frozen seasonally (Zhang et al., 2003). However, due to global warming, the snowpack on the soil surface become thinner and thinner, which will reduce its thermal insulation capability during FTCs (Du et al., 2020). If the increase in the frequency of FTCs can destroy soil aggregates, organic carbon contained in them will be available to microorganisms, which will eventually shake the balance between soil

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<https://doi.org/10.1016/j.geoderma.2021.115514>

Received 26 April 2021; Received in revised form 24 September 2021; Accepted 29 September 2021

Available online 9 October 2021

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carbon and atmospheric carbon.

The impact of FTCs on the stability of soil aggregate has recently attracted more and more attention. Some researchers have found that FTCs promote fragmentation and reduce the stability of soil aggregate by breaking down large soil aggregates into smaller ones (Edwards, 1991; Ma et al., 2020; Wang et al., 2012), while others refuted this, suggesting that FTCs may essentially promote aggregation by generating more soil aggregates (Lehrsch, 1998; Žabenská and Dumbrovský, 2015). In addition, an in-depth study by Li and Fan (2014) found that FTCs exhibit opposite effects on large or small soil aggregates. The frequency of FTCs is also important, Oztas and Fayetorbay (2003) found that soil aggregates become more stable after three to six FTCs. Although it is a highly heterogeneous system containing various types of soil aggregates and a large number of independent mineral particles, soil collected from a certain region is the most popular sample for studying the relationship between the stability of soil aggregate and FTCs (Edwards, 1991; Kværnø and Øygarden, 2006; Lehrsch et al., 1991; Lehrsch, 1998; Li and Fan, 2014; Ma et al., 2020; Mostaghimi et al., 1988; Oztas and Fayetorbay, 2003; Wang et al., 2012; Žabenská and Dumbrovský, 2015). So far, there are few characterizations of the structure and composition of the aggregates formed by suspended organic matter coated mineral particles under FTCs. In view of this, we are motivated to zoom out our focus in a whole soil sample and select a specific pair of host minerals and organic agents to study the initial formation of soil aggregates under simulated FTCs.

Iron (hydr)oxide are the essential components of soil aggregates (Xue et al., 2019). Some researchers had shown that organic matter coated iron (hydr)oxides particles (e.g., goethite, hematite and magnetite) can spontaneously form aggregates (Arce et al., 2017; Dultz et al., 2018; Illés and Tombácz, 2006; Zhang and Buffle, 1995), while others believed that organic matter coated iron (hydr)oxides particles can stably suspend in the solution (Hufschmid et al., 2017; Li et al., 2020; Zhao et al., 2018). In general, the aggregation process is greatly affected by the surface charge of the organic matter coated iron (hydr)oxides particles. Here, we chose goethite (α -FeOOH) as the model mineral because goethite is not only widely distributed but also stable in the natural soil environment (Hu et al., 2016; Liu et al., 2014). Due to its large surface area and high surface reactivity, goethite plays a central role in the migration and transformation of contaminants in soils (Hou et al., 2017; Zhu et al., 2017). And the positively charged surface of goethite makes it easy to bind natural organic matter in most soils (Weng et al., 2006). Humic acid (HA) is one of the most abundant fractions of natural organic matter and the main binding agent for the formation of soil aggregates (Chaney and Swift, 1986; Stevenson, 1994). Therefore, the use of HA extracted from natural soil as a binding agent for soil aggregates can better simulate the initial aggregation under the influence of freeze–thaw. The abundant surface functional groups on the surface of goethite can facilitate the adsorption of HA through ligand exchange, hydrophobic interaction, hydrogen bonding, chelation and cation bridging (Kaiser and Guggenberger, 2007; Philippe and Schaumann, 2014). The adsorption of HA molecules on the surface of goethite will generate negatively charged HA-coated goethite (goethite-HA) particles, which are stable in suspension and difficult to physically aggregate due to the electrostatically repulsion between them (Hufschmid et al., 2017; Li et al., 2020; Zhao et al., 2018). Whether these stable goethite-HA particles will aggregate under the effect of FTCs is still unknown.

In this study, we observed for the first time that suspended goethite-HA particles can form aggregates after a single freeze–thaw cycle. The morphology and elemental composition of the aggregates were studied by microscopic and elemental analysis. Then we performed bonding and thermodynamical analysis to evaluate the aggregation mechanism. By selecting goethite as the representative soil mineral and HA as the representative soil organic matter, this work attempts to introduce a new aggregation pathway for the evolution of soil aggregates in iron (hydr)oxide-rich soils under FTCs and explain its underlying mechanism.

2. Materials and methods

2.1. Preparation of humic acid

HA was extracted from a yellow–brown soil, one of the major soils in the karst region of southwest China. The soil sample was taken from the surface (0–50 cm) of a hilltop in the high-altitude area of west Guizhou, where FTCs often occur in winter. HA extraction followed the recommended method of the International Humic Substance Society (IHSS) and was described in detail elsewhere (Di et al., 2019). Briefly, the soil sample (100 g) was extracted with 400 ml NaOH (0.5 mol L^{-1}) under N_2 atmosphere and gently shaken for 12 h at room temperature ($20 \pm 1 \text{ }^\circ\text{C}$). The suspension was centrifuged at 3500 rpm for 20 min, and then the supernatant was collected. The collected supernatant was acidified to pH 1.0 with HCl (6 mol L^{-1}) to induce HA precipitation. The dissolution and precipitation of HA were repeated five times, and then the HA was demineralized by 10 ml HCl (0.1 mol L^{-1})-HF (0.3 mol L^{-1}) solution. The HA was repeatedly washed with Milli-Q water and then freeze-dried. The HA stock solution (100 mg L^{-1}) was prepared by suspending 50 mg purified HA powder in 500 ml NaCl solution (0.05 mol L^{-1}). The excitation-emission spectra (F-4600, Hitachi, Japan) and UV–vis spectra (U-3010, Hitachi High Technologies Co., Japan) of HA are given in Fig. S1 and S2 respectively. The molecular weight distribution of HA was measured using size exclusion chromatography (SEC, Alliance 2695, Waters Corp., USA) equipped with an UV/Visible detector (Fig. S3). The element content, ash content and carboxyl concentration are listed in Table S1.

2.2. Synthesis of goethite crystals

Goethite (α -FeOOH) crystals were synthesized according to the procedure described by Schwertmann and Cornell (2008). First, we dissolved 50 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 825 ml Milli-Q water under N_2 atmosphere and continuously stirred at room temperature ($20 \pm 1 \text{ }^\circ\text{C}$). Then, NaOH (5 mol L^{-1}) was slowly added into this solution until the pH of 12 was reached. The obtained suspension was aged at $60 \text{ }^\circ\text{C}$ for 48 h and then centrifuged. The precipitate was washed with Milli-Q water until the conductivity was lower than $3 \mu\text{S cm}^{-1}$. Finally, the goethite was dried at $60 \text{ }^\circ\text{C}$ and ground to powder. The synthesized goethite sample was analyzed using powder X-ray diffraction (XRD, X'Pert PRO MPD, PANalytical, Netherlands) to determine the crystal structure. A Fourier transform infrared spectrometer (FTIR, Bruker VERTEX 70, Germany) was used to obtain the spectrum of synthesized goethite. We performed scanning electron microscopy (SEM, SU-8020, HITACHI, Japan) and transmission electron microscopy (TEM, JEM-2100F, JEOL) to characterize the morphology. The initial screening of the goethite crystals is shown in Fig. S4. The goethite suspension (100 mg L^{-1}) was prepared by adding 100 mg synthesized goethite powder to 1 L NaCl solution (0.05 mol L^{-1}).

2.3. Adsorption procedure

The adsorption of HA on goethite was carried out in NaCl solution (0.05 mol L^{-1}), and the pH was adjusted to 7.00 ± 0.02 by using HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}). The mass ratio of HA to goethite was set to 1:5 (see Fig. S5) by mixing 100 ml HA stock solution and 500 ml goethite suspension in a 1 L glass bottle and the adsorption time of HA on goethite was set to 24 h to ensure the saturated adsorption of HA on the surface of goethite. After complete mixing, the suspension was shaken at 100 rpm using a shaker at room temperature ($20 \pm 1 \text{ }^\circ\text{C}$) for 24 h. Once the adsorption completed, the suspension was centrifuged at 14,000 rpm for 10 min, and the supernatant was removed. The precipitate (goethite-HA) was dried in an oven at $60 \text{ }^\circ\text{C}$, and then ground into powder for the following freeze–thaw experiment.

2.4. Freeze-thaw experiment of goethite-HA

The goethite-HA suspension (100 mg L^{-1}) was prepared by mixing 4 mg goethite-HA powder and 40 ml Milli-Q water in a 50 ml centrifuge tube (polypropylene). In order to ensure that all the goethite-HA particles had been suspended in water, the ultrasonic treatment (ultrasound condition: 200 W and 20 KHz) was used to treat the aqueous suspension until there was no agglomeration. The Zeta potential values of goethite-HA and goethite suspensions were measured by using a Zetasizer Nano ZS90 (Malvern Instruments, Malvern, UK). The suspension was frozen at -24°C for 12 h and thawed at 4°C for another 12 h as one freeze-thaw cycle. In order to obtain sufficient goethite-HA aggregates, six parallel goethite-HA suspensions were employed in the freeze-thaw experiment. For comparison, a goethite suspension (100 mg L^{-1}) was also treated with the same freeze-thaw procedure and a goethite-HA suspension was simply stored at 4°C for 24 h.

2.5. Characterization of goethite-HA aggregates

After one freeze-thaw cycle treatment, all the goethite-HA precipitates were collected and dried in an air-circulating oven at 60°C for 12 h. TEM and SEM were used to check the morphology of the precipitates. The elemental mapping of the precipitates was done by TEM-Energy Dispersive X-ray Analysis (TEM-EDX). The size distribution of the precipitates was determined by a manual wet sieving method (Six et al., 2002) to evaluate the particle size fractions of $< 20 \mu\text{m}$, $20\text{--}53 \mu\text{m}$, $53\text{--}250 \mu\text{m}$, and $250\text{--}2000 \mu\text{m}$ (description of the wet sieving method is listed in Supplementary Materials). To test whether the crystal structure of goethite particle changed after the freeze-thaw treatment, the goethite-HA precipitates was studied by XRD. The thermal stability of the goethite-HA particles was tested by thermogravimetric analysis (TGA) before and after the freeze-thaw experiment. The goethite-HA sample was heated to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ in flowing air. The elemental composition (C and H) of goethite-HA before and after the freeze-thaw experiment was determined with an elemental analyzer (Elementar Vario EL III, Germany). Fourier transform infrared spectroscopy (FTIR) spectrum was measured for goethite-HA particle at all stages of the experiment to further understand the effects of freezing and thawing. Briefly, a pressed pellet mixture of 10 mg dry goethite-HA powder (with or without the freeze-thaw treatment) and 100 mg KBr powder (FTIR grade, Sigma-Aldrich) was prepared and used for the measurement on a FTIR spectrometer (Bruker VERTEX 70, Germany).

3. Results and discussion

3.1. Adsorption of HA on goethite

The adsorption of HA on goethite was carried out to trigger the formation of the goethite-HA complex, which is considered to be the precursor for the formation of soil aggregates (Vindedahl et al., 2016). The successful adsorption of HA on goethite is usually manifested by the formation of new bonds between the carboxyl groups of HA and iron atoms on the surface of the goethite (Gu et al., 1995). The change of Zeta potential before and after the adsorption experiment can confirm that HA molecules have been adsorbed on the surface of goethite. For example, the net surface charge of the goethite-HA complex is negative (Zeta potential $-32 \pm 1 \text{ mV}$) while the net surface charge of the goethite is positive (Zeta potential $44 \pm 1 \text{ mV}$) at pH 7.00 in this study. According to FTIR spectra (Fig. 1), the goethite-HA complex shows the vibrational modes of HA and goethite. Both goethite and goethite-HA show IR peaks at 1655 cm^{-1} ($\gamma\text{OH} + \delta\text{OH}$) and 1792 cm^{-1} (δ_{OH}), which refer to the water bending bands (Boily and Felmy, 2008; Boily et al., 2006), and these water molecules were adsorbed on the surface of the goethite (Liu et al., 2013). It is worth noting that the band at 1625 cm^{-1} is attributed to both the aromatic C=C vibrational mode and the carboxyl-iron bond

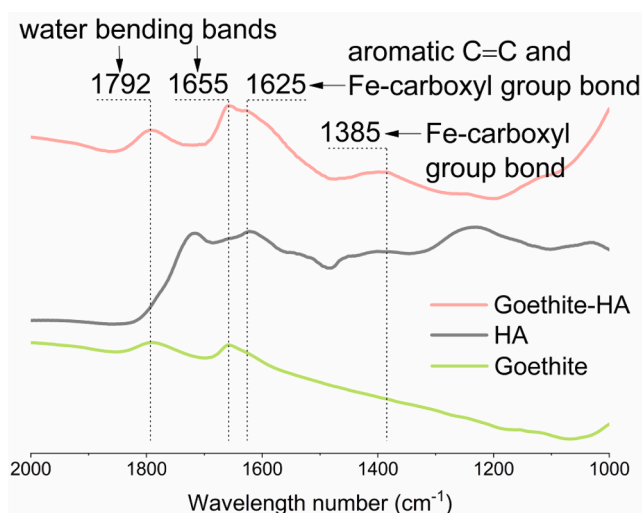


Fig. 1. FTIR spectra of goethite, HA and goethite-HA.

formed by ligand exchange (Gu et al., 1994). Nevertheless, the peak at 1385 cm^{-1} was only observed in goethite-HA, which clearly indicated the complexation between HA and goethite (Gu et al., 1994; Gu et al., 1995).

3.2. Impact of freeze-thaw on goethite-HA

As shown in Fig. 2, after one freeze-thaw cycle, a large amount of precipitation (greater than 97 wt%) was observed in the goethite-HA suspension tube (Fig. 2 a1 and a2). In sharp contrast to this, the pure goethite suspension undergoing the same freeze-thaw cycle (Fig. 2 b1 and b2) and the goethite-HA suspension stored at 4°C for 24 h without the freeze-thaw treatment (Fig. 2 c1 and c2) did not form any precipitates, both the pure goethite and goethite-HA were stable and did not aggregate in suspension. We speculated that the ice exclusion in the freezing step is the main reason for triggering the above observed phenomenon. The suspended goethite and goethite-HA particles were squeezed into the center of the centrifuge tube under the action of ice exclusion, which laid the foundation for the subsequent aggregation of goethite-HA particles. The characterization results of the suspension and texture further showed that only HA-coated goethite precipitated, indicating that HA as a binding agent to connect goethite particles may be another mechanism for the formation goethite-HA aggregates after a single freeze-thaw cycle.

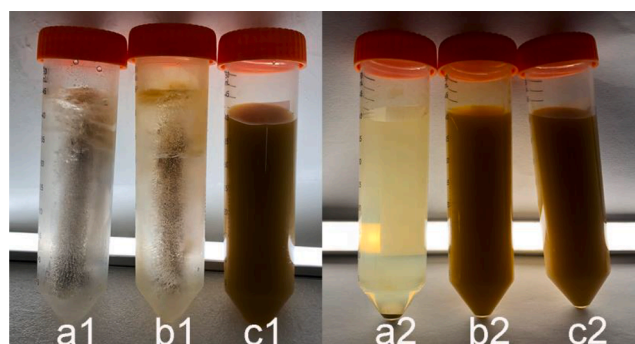


Fig. 2. Suspended samples with and without treatment of freeze-thaw. a1, goethite-HA suspension was frozen for 12 h. b1, goethite suspension was frozen for 12 h. c1, goethite-HA suspension was preserved at 4°C for 12 h. a2, goethite-HA suspension was thawing for 12 h. b2, goethite suspension was thawing for 12 h. c2, goethite-HA suspension was then preserved at 4°C for another 12 h.

3.3. Characterization of goethite-HA aggregates

Our experiments showed that freeze–thaw helped the suspended goethite-HA particles to aggregate. SEM analysis revealed that after one freeze–thaw cycle, the goethite-HA suspension produced not only a small amount of individual goethite particles, but also a large number of aggregates of different sizes and morphologies (Fig. S6). In Fig. 3a–c, we randomly selected and zoomed in a certain aggregate. More details showed up with the increase of magnification and the lump was found to be composed of packed needle-shaped goethite crystals that are likely goethite-HA aggregates. We further verified the goethite-HA aggregate by the TEM-EDX elemental mapping (Fig. 3d–g). Here, we used nitrogen instead of carbon as the primary probe for detecting the aggregate, not only because our HA sample contains 4.18 wt% nitrogen (Table S1), but also because the carbon signal will be invalid when using the carbon film-coated copper grid (Fig. 3e). The EDX mapping shows that the Fe and N concentrations in the center area of the aggregate vary consistently, indicating that a considerable part of HA is enclosed in the goethite-HA aggregate. In addition, the results of wet sieving indicated that most of goethite-HA aggregates are 53–250 μm in size (Fig. 4), which was reported to be a favorable size for capturing organic carbon (Six et al., 2004).

In Fig. 5a, the TGA results clearly show that the weight loss of goethite-HA aggregates obtained after one freeze–thaw cycle was greater than that of goethite-HA particles that had not been subjected to the freeze–thaw treatment. Because water was the only other reactant in the centrifuge tube, we attributed this to additional water molecules had been involved in the aggregation of goethite-HA during the freeze–thaw process, because the surface of goethite-HA can adsorb a thin water film (Song and Boily, 2013). This is also supported by the increased hydrogen content in the goethite-HA aggregates (table in Fig. 5b). The adsorption of additional water molecules was further supported by FTIR results (Fig. 5c), where we found that both water bending (1655 cm^{-1} and 1792 cm^{-1}) and carboxyl-iron binding (1385 cm^{-1} and 1625 cm^{-1}) bands of goethite-HA after freeze–thaw were simultaneously strengthened. For example, the absorbance measured by peak heights at 1385 cm^{-1} and 1625 cm^{-1} increased by 84% and 32%, respectively. Meanwhile, the absorbance peak of the Fe-O band at 642 cm^{-1} had the same height. The significant strengthening of peaks located between 1200 cm^{-1} and 1800 cm^{-1} is mainly due to the stronger chemical interaction between the goethite-HA particles. The XRD patterns of the three samples are consistent (Fig. 5d), and the perfectly matched diffraction peaks indicates that the freeze–thaw action did not affect the integrity of the goethite structure. It is possible that those additional water molecules may act as proton donors and form hydrogen bonds between goethite-HA particles (Filius et al., 1997), thereby increasing the size of the goethite-HA aggregates. It is worth noting that both FTIR and TGA experiments consistently show that the goethite-HA aggregates contained more water compared with individual goethite-HA particles, and then formed additional hydrogen bonds on the surface of the goethite. Freeze–thaw may promote the formation of new chemical bonds by helping overcome electrostatic repulsion and steric hindrance, which are generally considered to be the main factors in preventing the aggregation of goethite-HA particles (Domingos et al., 2009; Li et al., 2020;

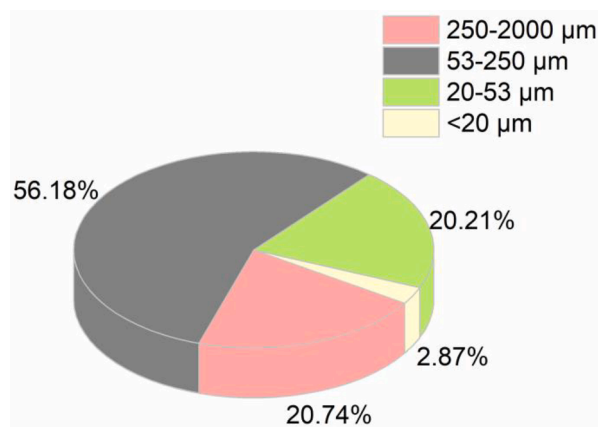


Fig. 4. The particle size distribution of goethite-HA aggregates in wt.%.

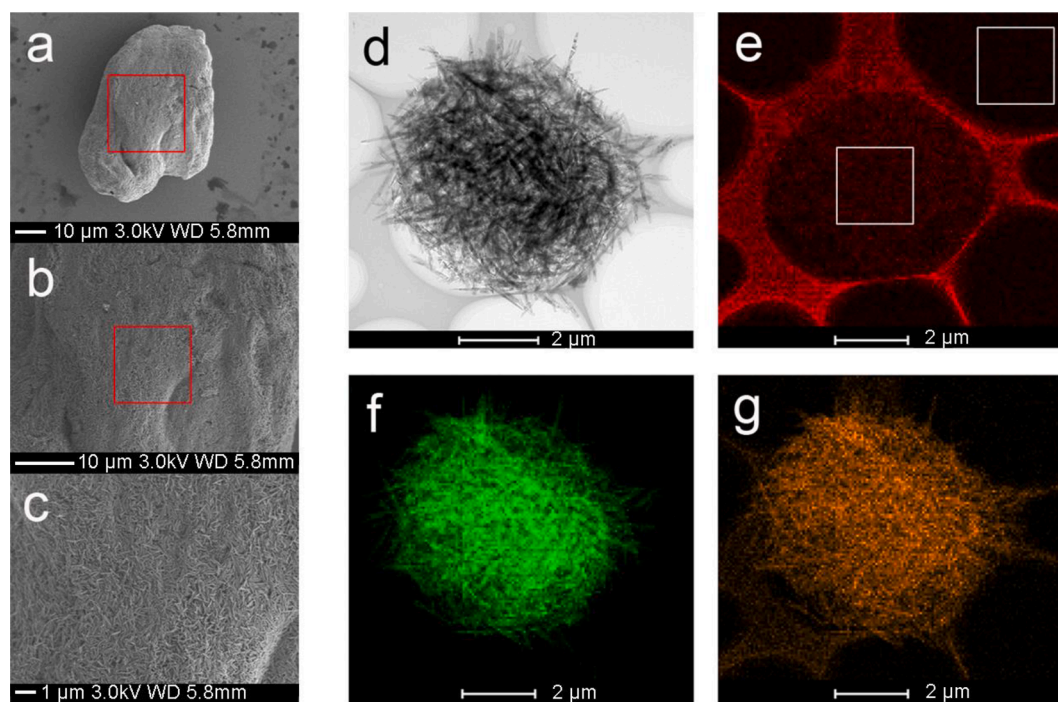


Fig. 3. The composition and morphology of goethite-HA aggregates. a–c zoom-in SEM image of a goethite-HA aggregate. the magnification gradually increased from a to c. d, TEM image of a goethite-HA aggregate. The grey areas are thin carbon films. e–g, TEM-EDX element maps for C (e), Fe (f) and N (g) respectively. The high C concentration in e is due to the thin carbon films.

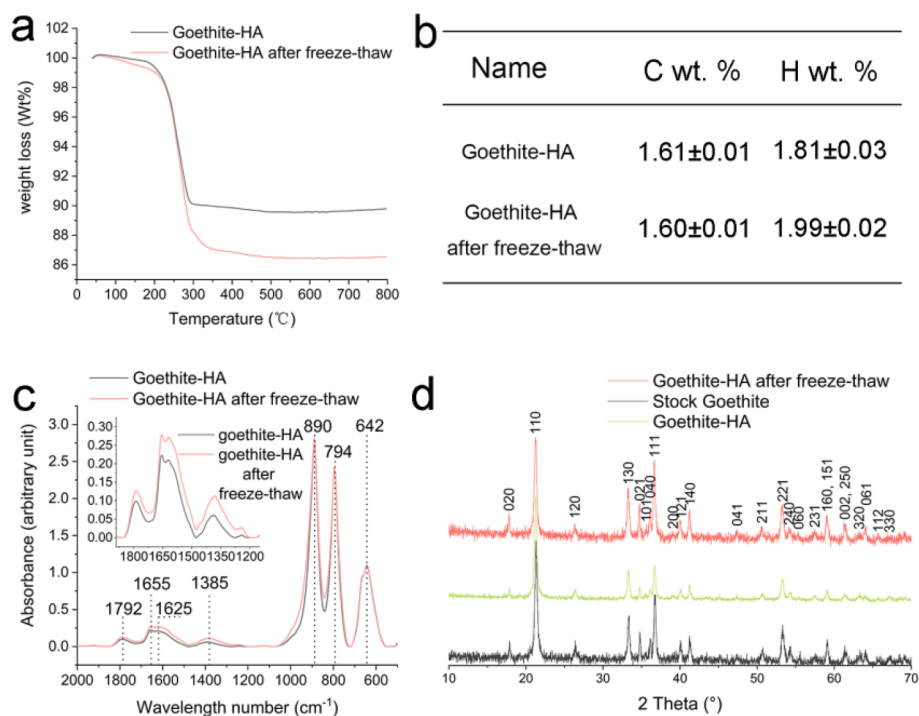


Fig. 5. Characterization of goethite-HA aggregates. a, The TGA traces for goethite-HA before and after freeze-thaw. b, C and H content of goethite-HA and goethite-HA after freeze-thaw. c, FTIR absorption spectra showing the strengthened OH bonding (1655 and 1792 cm^{-1}). In order to show the change of peak intensity more clearly, we magnified the specific region as an inset. d, XRD patterns of goethite-HA before and after freeze-thaw and stock goethite.

Vindedahl et al., 2016).

3.4. Aggregation of goethite-HA particles

The electrostatic repulsion and steric hindrance are factors to hinder the aggregation of suspended organic matter coated mineral particles in soil solutions (Li et al., 2020; Ma et al., 2018). As we all know, mineral particles coated with organic matter can form aggregates through their own Brownian motion (Banfield et al., 2000). However, Brownian motion is highly correlated with the molecular weight of adsorbed organic molecules. For example, the aggregation of organic matter-coated mineral particles is mainly restricted by steric hindrance rather than electrostatic repulsion when the molecular weight of adsorbed organic matter is below 3 kDa (Li et al., 2020). The molecular weight distribution of our HA ranged from 500 Da to 73 kDa, and only a very small part of HA had a molecular weight below 3 kDa (Fig. S3). In view of this, the electrostatic repulsive force between the suspended goethite-HA particles is difficult to overcome by Brownian motion in this study. We speculated that if it exists, the role of Brownian motion in the aggregation of suspended goethite-HA particles is not so important. Previous reports indicated that the freeze-thaw cycle usually destroyed aggregates due to the volume expansion of pore water in freezing (Lehrsch et al., 1991). However, this work suggested that ice exclusion may play a key role in the growth of goethite-HA aggregates during freeze-thaw. The freeze-thaw experiment showed when the goethite-HA suspension started to freeze, ice crystals were formed from the outer layer to the inner layer of the centrifuge tube, the ice crystals squeezed the suspended goethite and goethite-HA particles into the center of the tube. The physical squeezing force can overcome the electrostatic repulsion and steric hindrance between goethite and goethite-HA particles and shorten the distance between them. Once the surface charge density of these particles overlaps to a sufficient degree, chemical bonds can form, and the suspended particles begin to aggregate. In short, our experiment showed that ice exclusion disturbed the electrostatic balance between goethite-HA particles during freeze-thaw cycle, so their reaction

surfaces could be fully utilized to form chemical bonds for aggregation (Fig. 2b).

3.5. The extra formation of chemical bonds

From a chemical point of view, we characterized two types of chemical bonding in the formation of goethite-HA aggregate: namely, the carboxyl-iron and the hydrogen bonding, both of which can connect adjacent goethite particles. The carboxyl-iron bonding may be achieved by ligand exchange, that is, carboxyl groups of HA bind to Fe atoms of the surface of goethite, while the hydrogen bonding is due to the formation of hydrogen bonds between the HA molecules in the goethite-HA particles, which connects the goethite-HA particles to each other. The formation of both types of chemical bonds may be the driving force to grow the size of goethite-HA aggregates.

3.6. The fate of those formed goethite-HA aggregates

It was reported that the repeated FTCs can promote the fragmentation of soil aggregates by breaking down the large soil aggregate into smaller ones (Ma et al., 2020). Consequently, a part of those formed goethite-HA aggregates may be fragmented in following FTCs. It has not escaped from our notice that the fragmentation of goethite-HA aggregates may release a portion of goethite-HA particles to resuspend in water. However, those suspended goethite-HA particles will be influenced by the ice exclusion and aggregated again under freezing. To sum up, the formation and fragmentation of aggregate may occur simultaneously under repeated FTCs. The fate of aggregates upon repeated cycles is controlled by the combined factors of freezing and thawing temperature, which will lead to a future comprehensive study.

3.7. Environmental implications

In highly heterogeneous soil systems, goethite, due to its highly reactive surface, may play significant roles in the aggregation process

and contribute a large share in adsorbing organic carbon compounds. The contradictory results in the literature regarding the stability of soil aggregate under FTCs may be due to their different chemical composition, such as the iron (hydr)oxides content. For example, the stability of aggregates in soils rich in iron (hydr)oxides is usually better than that in soils lacking iron (hydr)oxides under FTCs. In soils lacking iron (hydr)oxides, FTCs may likely destroy more soil aggregates (Edwards, 1991), causing soil aggregates to release organic carbon. The organic carbon released by soil aggregates can be easily utilized by soil microorganisms, and therefore enhance the emission of soil carbon to the atmosphere. Previous understanding of the effect of ice crystals during FTCs is mainly that the volume expansion of ice crystals destroys soil aggregates. However, our results showed that ice exclusion can cause suspended goethite-HA particles to form aggregates, thereby enclosing organic matters and protecting them from decomposition. This mechanism may be particularly important in controlling CO₂ emissions from soil near the climatic snow line where FTC often occurs.

3.8. Experiment limitation

In this study, we focused on whether suspended goethite-HA particles aggregate under freeze–thaw and the aggregation mechanism. We tested the goethite-HA suspension with only one single freeze–thaw cycle and did not further study the fate of newly formed aggregates after multiple FTCs. This will continue to be explored in the follow-up work. Besides goethite and HA, aggregation behaviors of other soil minerals and soil organic carbon, such as hematite and dissolved organic matters, were not tested in this study. All these limited the estimation of the importance of goethite-HA aggregates in sequestering organic carbon in natural soils. Our experiment was conducted at pH 7, the pH of most soils (Magdoff and Bartlett, 1985), but it had been suggested that the adsorption of HA on goethite surface is sensitively affected by the pH (Weng et al., 2006). Therefore, it is necessary to further study the aggregation of goethite-HA (or hematite-HA) under freeze–thaw at different pH values and freezing temperatures.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was financially supported by the Strategic Priority Research Program of Chinese Academy of Sciences (XDB40020400) and the National Science Foundation of China (41773147, 41273149). Q.H. is supported by the CAEP Research Project (CX20210048) and Tencent Explorer Prize. The Center for High Pressure Science and Technology Advanced Research (HPSTAR) operations are partially supported by NSAF (Grant No: U1530402). We want to acknowledge Freyja O'Toole for her help proofreading the manuscript. We acknowledge Susanne Karoline Woche and other anonymous reviewers for their constructive and enlightened comments in the reviewing process.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2021.115514>.

References

Arce, G., Montecinos, M., Guerra, P., Escauriza, C., Coquery, M., Pastén, P., 2017. Enhancement of particle aggregation in the presence of organic matter during neutralization of acid drainage in a stream confluence and its effect on arsenic immobilization. *Chemosphere* 180, 574–583.

- Banfield, J.F., Welch, S.A., Zhang, H., Ebert, T.T., Penn, R.L., 2000. Aggregation-based crystal growth and microstructure development in natural iron oxyhydroxide biomineralization products. *Science* 289, 751–754.
- Boily, J.-F., Felmy, A.R., 2008. On the protonation of oxo- and hydroxo-groups of the goethite (α -FeOOH) surface: A FTIR spectroscopic investigation of surface O-H stretching vibrations. *Geochim. Cosmochim. Acta* 72 (14), 3338–3357.
- Boily, J.-F., Szanyi, J., Felmy, A.R., 2006. A combined FTIR and TPD study on the bulk and surface dehydroxylation and decarbonation of synthetic goethite. *Geochim. Cosmochim. Acta* 70 (14), 3613–3624.
- Bronick, C.J., Lal, R., 2005. Soil structure and management: a review. *Geoderma* 124, 3–22.
- Chaney, K., Swift, R., 1986. Studies on aggregate stability. The effect of humic substances on the stability of re-formed soil aggregates. *J. Soil Sci.* 37, 337–343.
- Di, X., Xiao, B., Dong, H., Wang, S., 2019. Implication of different humic acid fractions in soils under karst rocky desertification. *Catena* 174, 308–315.
- Domingos, R.F., Tufenkji, N., Wilkinson, K.J., 2009. Aggregation of titanium dioxide nanoparticles: role of a fulvic acid. *Environ. Sci. Technol.* 43, 1282–1286.
- Du, L., Dyck, M., Shoty, W., He, H., Lv, J., Cuss, C.W., Bie, J., 2020. Lead immobilization processes in soils subjected to freeze-thaw cycles. *Ecotox. Environ. Saf.* 192, 110288.
- Dultz, S., Steinke, H., Mikutta, R., Woche, S.K., Guggenberger, G., 2018. Impact of organic matter types on surface charge and aggregation of goethite. *Colloids Surf. A* 554, 156–168.
- Edwards, L., 1991. The effect of alternate freezing and thawing on aggregate stability and aggregate size distribution of some Prince Edward Island soils. *J. Soil Sci.* 42, 193–204.
- Filius, J.D., Hiemstra, T., Van Riemsdijk, W.H., 1997. Adsorption of small weak organic acids on goethite: Modeling of mechanisms. *J. Colloid Interface Sci.* 195, 368–380.
- Goebel, M.-O., Bachmann, J., Woche, S.K., Fischer, W.R., 2005. Soil wettability, aggregate stability, and the decomposition of soil organic matter. *Geoderma* 128, 80–93.
- Gu, B., Schmitt, J., Chen, Z., Liang, L., McCarthy, J.F., 1994. Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. *Environ. Sci. Technol.* 28 (1), 38–46.
- Gu, B., Schmitt, J., Chen, Z., Liang, L., McCarthy, J.F., 1995. Adsorption and desorption of different organic matter fractions on iron oxide. *Geochim. Cosmochim. Acta* 59, 219–229.
- Guan, S., An, N., Zong, N., He, Y., Shi, P., Zhang, J., He, N., 2018. Climate warming impacts on soil organic carbon fractions and aggregate stability in a Tibetan alpine meadow. *Soil Biol. Biochem.* 116, 224–236.
- Harris, R., Chesters, G., Allen, O., 1966. Dynamics of soil aggregation. *Adv. Agron. Elsevier* 18, 107–169.
- Hou, X., Huang, X., Jia, F., Ai, Z., Zhao, J., Zhang, L., 2017. Hydroxylamine promoted goethite surface Fenton degradation of organic pollutants. *Environ. Sci. Technol.* 51, 5118–5126.
- Hu, Q., Kim, D.Y., Yang, W., Yang, L., Meng, Y., Zhang, L., Mao, H.-K., 2016. FeO₂ and FeOOH under deep lower-mantle conditions and Earth's oxygen–hydrogen cycles. *Nature* 534, 241–244.
- Hufschmid, R., Newcomb, C.J., Grate, J.W., De Yoreo, J.J., Browning, N.D., Qafoku, N.P., 2017. Direct visualization of aggregate morphology and dynamics in a model soil organic–mineral system. *Environ. Sci. Technol. Lett.* 4, 186–191.
- Illés, E., Tombácz, E., 2006. The effect of humic acid adsorption on pH-dependent surface charging and aggregation of magnetite nanoparticles. *J. Colloid Interface Sci.* 295, 115–123.
- Jastrow, J.D., 1996. Soil aggregate formation and the accrual of particulate and mineral-associated organic matter. *Soil Biol. Biochem.* 28, 665–676.
- Kaiser, K., Guggenberger, G., 2007. Sorptive stabilization of organic matter by microporous goethite: sorption into small pores vs. surface complexation. *Eur. J. Soil Sci.* 58, 45–59.
- Kværnø, S.H., Øygarden, L., 2006. The influence of freeze–thaw cycles and soil moisture on aggregate stability of three soils in Norway. *Catena* 67, 175–182.
- Lal, R., 2004. Soil carbon sequestration impacts on global climate change and food security. *Science* 304, 1623–1627.
- Lehrsch, G.A., 1998. Freeze-thaw cycles increase near-surface aggregate stability. *Soil Sci.* 163, 63–70.
- Lehrsch, G.A., Sojka, R.E., Carter, D.L., Jolley, P.M., 1991. Freezing effects on aggregate stability affected by texture, mineralogy, and organic matter. *Soil Sci. Soc. Am. J.* 55, 1401–1406.
- Li, G.-Y., Fan, H.-M., 2014. Effect of freeze-thaw on water stability of aggregates in a black soil of Northeast China. *Pedosphere* 24 (2), 285–290.
- Li, Z., Shakiba, S., Deng, N., Chen, J., Louie, S.M., Hu, Y., 2020. Natural organic matter (NOM) imparts molecular-weight-dependent steric stabilization or electrostatic destabilization to ferrihydrite nanoparticles. *Environ. Sci. Technol.* 54, 6761–6770.
- Liu, H., Chen, T., Qing, C., Xie, Q., Frost, R.L., 2013. Confirmation of the assignment of vibrations of goethite: An ATR and IES study of goethite structure. *Spectrochim. Acta A* 116, 154–159.
- Liu, H., Chen, T., Frost, R.L., 2014. An overview of the role of goethite surfaces in the environment. *Chemosphere* 103, 1–11.
- Ma, J., Guo, H., Lei, M., Li, Y., Weng, L., Chen, Y., Ma, Y., Deng, Y., Feng, X., Xiu, W., 2018. Enhanced transport of ferrihydrite colloid by chain-shaped humic acid colloid in saturated porous media. *Sci. Total Environ.* 621, 1581–1590.
- Ma, R., Jiang, Y., Liu, B., Fan, H., 2020. Effects of pore structure characterized by synchrotron-based micro-computed tomography on aggregate stability of black soil under freeze-thaw cycles. *Soil Tillage Res.* 207, 104855.
- Magdoff, F.R., Bartlett, R.J., 1985. Soil pH buffering revisited. *Soil Sci. Soc. Am. J.* 49, 145–148.

- Mostaghimi, S., Young, R.A., Wilts, A., Kenimer, A., 1988. Effects of frost action on soil aggregate stability. *Trans. ASAE* 31, 435–4439.
- Oztas, T., Fayetorbay, F., 2003. Effect of freezing and thawing processes on soil aggregate stability. *Catena* 52, 1–8.
- Philippe, A., Schaumann, G.E., 2014. Interactions of dissolved organic matter with natural and engineered inorganic colloids: a review. *Environ. Sci. Technol.* 48, 8946–8962.
- Schwertmann, U., Cornell, R.M., 2008. *Iron Oxides in the Laboratory: Preparation and Characterization*. John Wiley & Sons.
- Six, J., Conant, R.T., Paul, E.A., Paustian, K., 2002. Stabilization mechanisms of soil organic matter: implications for C-saturation of soils. *Plant Soil* 241, 155–176.
- Six, J., Bossuyt, H., Degryze, S., Deneff, K., 2004. A history of research on the link between (micro) aggregates, soil biota, and soil organic matter dynamics. *Soil Tillage Res.* 79, 7–31.
- Song, X., Boily, J.-F., 2013. Water vapor adsorption on goethite. *Environ. Sci. Technol.* 47, 7171–7177.
- Stevenson, F.J., 1994. *Humus Chemistry: Genesis, Composition, Reactions*. John Wiley & Sons.
- Tisdall, J.M., Oades, J.M., 1982. Organic matter and water-stable aggregates in soils. *J. Soil Sci.* 33, 141–163.
- Vindedahl, A.M., Stemig, M.S., Arnold, W.A., Penn, R.L., 2016. Character of humic substances as a predictor for goethite nanoparticle reactivity and aggregation. *Environ. Sci. Technol.* 50, 1200–1208.
- Wang, E., Cruse, R.M., Chen, X., Daigh, A., 2012. Effects of moisture condition and freeze/thaw cycles on surface soil aggregate size distribution and stability. *Can. J. Soil Sci.* 92, 529–536.
- Weng, L., Van Riemsdijk, W.H., Koopal, L.K., Hiemstra, T., 2006. Adsorption of humic substances on goethite: comparison between humic acids and fulvic acids. *Environ. Sci. Technol.* 40, 7494–7500.
- Xue, B., Huang, L.i., Huang, Y., Zhou, F., Li, F., Kubar, K.A., Li, X., Lu, J., Zhu, J., 2019. Roles of soil organic carbon and iron oxides on aggregate formation and stability in two paddy soils. *Soil Tillage Res.* 187, 161–171.
- Yang, C., Liu, N., Zhang, Y., 2019. Soil aggregates regulate the impact of soil bacterial and fungal communities on soil respiration. *Geoderma* 337, 444–452.
- Yu, X., Zou, Y., Jiang, M., Lu, X., Wang, G., 2011. Response of soil constituents to freeze–thaw cycles in wetland soil solution. *Soil Biol. Biochem.* 43, 1308–1320.
- Yudina, A., Kuzuyakov, Y., 2019. Saving the face of soil aggregates. *Glob. Change Biol.* 25, 3574–3577.
- Žabenská, A., Dumbrovský, M., 2015. Changes of soil aggregate stability as a result of the effect of freeze-thaw cycles. *Acta Univ. Agric. Silv. Mendelianae Brun* 63, 1211–1218.
- Zhang, T., Barry, R., Knowles, K., Ling, F., Armstrong, R., 2003. Distribution of seasonally and perennially frozen ground in the Northern Hemisphere. In: *Proceedings of the 8th International Conference on Permafrost*. AA Balkema Publishers Zürich, Switzerland, pp. 1289–1294.
- Zhang, J., Buffle, J., 1995. Kinetics of hematite aggregation by polyacrylic acid: Importance of charge neutralization. *J. Colloid Interface Sci.* 174, 500–509.
- Zhao, J., Chen, S., Hu, R., Li, Y., 2017. Aggregate stability and size distribution of red soils under different land uses integrally regulated by soil organic matter, and iron and aluminum oxides. *Soil Tillage Res.* 167, 73–79.
- Zhao, J., Giammar, D.E., Pasteris, J.D., Dai, C., Bae, Y., Hu, Y., 2018. Formation and aggregation of lead phosphate particles: Implications for lead immobilization in water supply systems. *Environ. Sci. Technol.* 52, 12612–12623.
- Zhu, S.-C., Hu, Q., Mao, W.L., Mao, H.-K., Sheng, H., 2017. Hydrogen-bond symmetrization breakdown and dehydrogenation mechanism of FeO₂H at high pressure. *J. Am. Chem. Soc.* 139, 12129–12132.