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# Interrogating organo-mineral interactions by Py-GC/MS and ToF-SIMS

September 2022

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## Abstract

Soil organic matter (SOM) is crucial to soil fertility and agricultural sustainability in the face of climate change, and organo-mineral interactions are a key mechanism for stabilizing SOM. The stability of mineral-associated organic matter (MAOM) can be approximated by the strength of bonds between biomolecules and mineral surfaces. We hypothesized that factors such as mineral reactivity and solution pH would impact bonding strength. To test these factors, sorption isotherms were performed on minerals differing in particle size, morphology, and reactivity (quartz, goethite, gibbsite, kaolinite, montmorillonite), under two pH conditions (4 and 6), and across a range of tannic acid (TA) concentration (0-1400 ppm). The quantity and quality of organo-mineral bonds was assessed by quantifying post-sorption solution compounds using an absorbance plate reader and assessing the thermal energy needed to break bonds using evolved gas analysis (EGA) on a pyrolysis gas chromatograph-mass spectrometer (Py-GC/MS). Organo-mineral surfaces were also interrogated using Time-of-flight secondary ion mass spectrometry (ToF-SIMS). Sorption experiments revealed an asymptotic relationship between sorbed TA and increasing initial concentrations which suggests our concentration range saturated available mineral surfaces. Results indicated that mineral identity, chiefly surface area and native pH, impacted the amount of compound sorbed to mineral surfaces. Evolved gas analyses of organo-mineral samples uncovered increased thermal stability of sorbed compounds compared to our TA standard particularly on the iron oxide, goethite. ToF-SIMS revealed that goethite surface ions were covered by increasing concentrations of adsorbed TA with the replacement of chlorine and sulfate ions by TA related ions. Our results indicate that Py-GC/MS and ToF-SIMS are useful techniques to determine the nature and strength of organo-mineral bonds and are steppingstones to understanding controls on carbon sequestration in terrestrial systems.

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## Figures

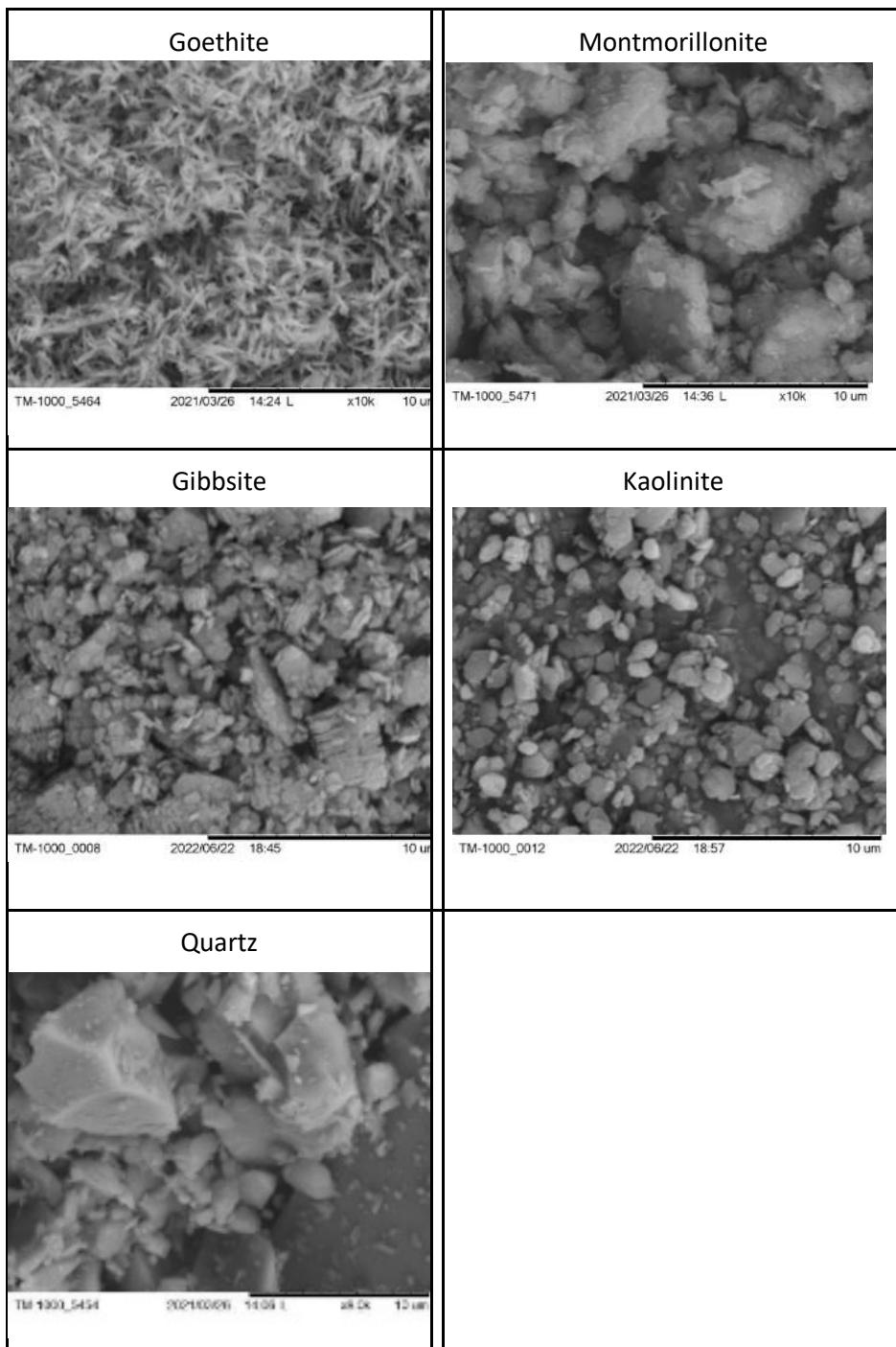


Figure 1: Scanning Electron Microscopy images of five minerals of interest.

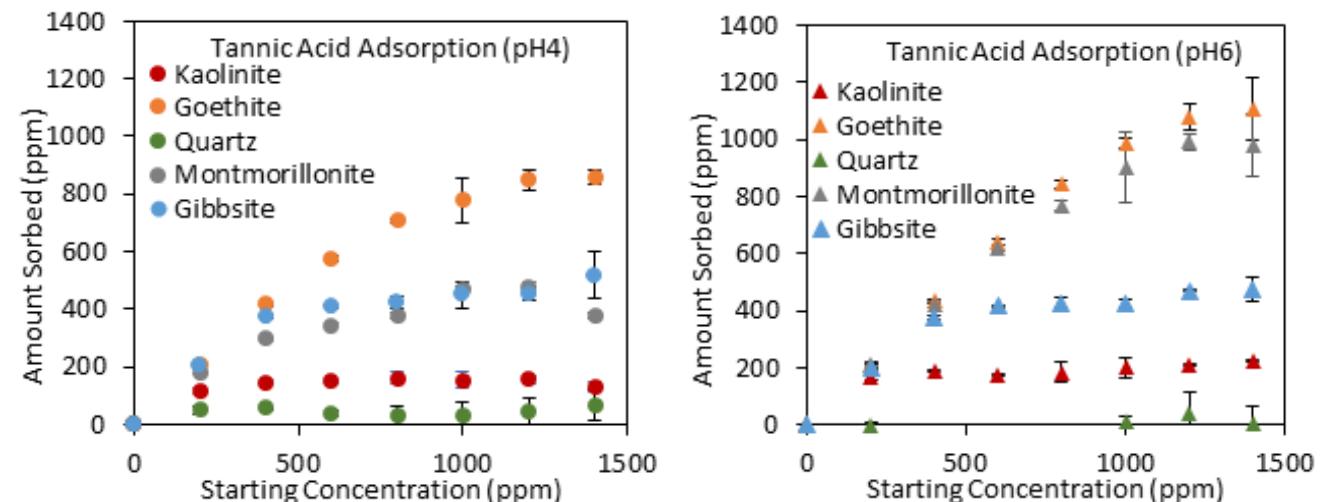


Figure 2: Adsorption kinetics of tannic acid on five mineral surfaces at pH 4 and 6.

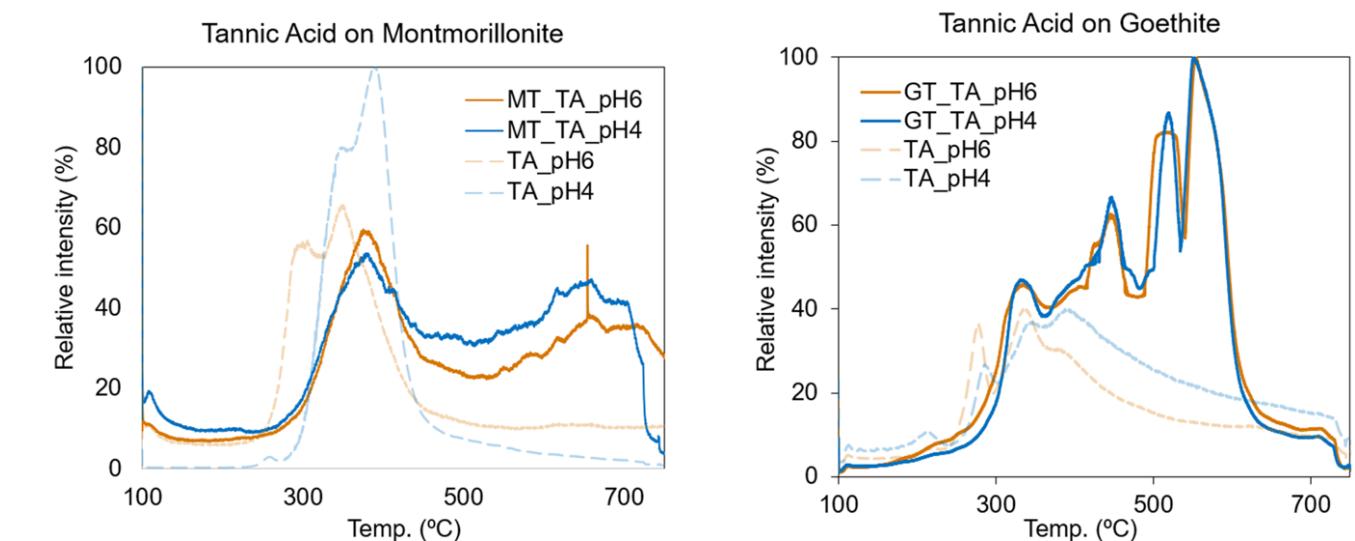


Figure 3: Pyrolysis evolved gas analysis (EGA) of tannic acid adsorbed to montmorillonite (MT) and goethite (GT) from 100-700 °C.

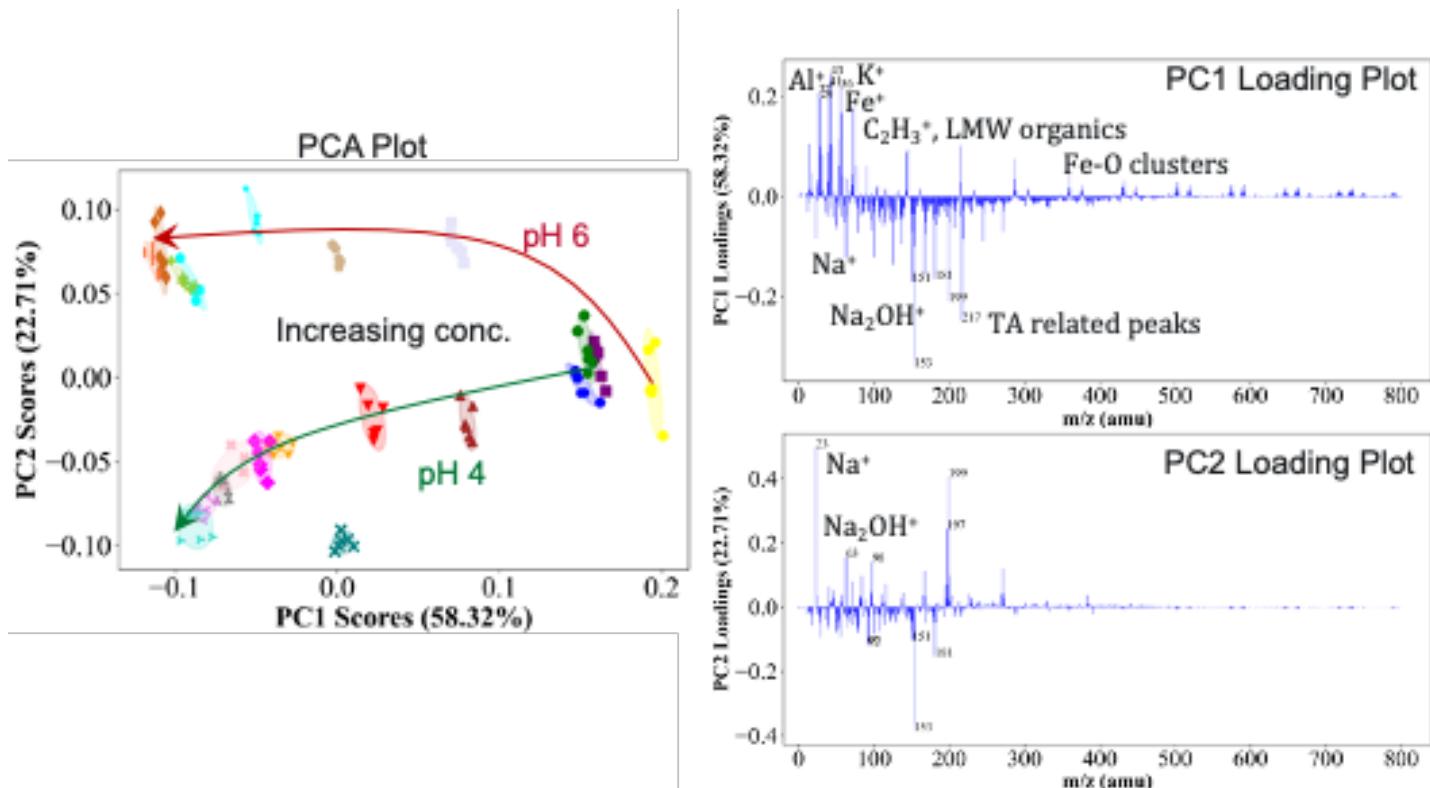


Figure 4: Time-of-flight secondary ion mass spectrometry results from tannic acid on goethite.

## Tables

Table 1: Properties of five minerals used in sorption experiments. Particle area was estimated from SEM images, surface area was measured by BET analysis, and initial pH was taken using a pH probe.

Mineral	Type	Particle Size ( $\mu\text{m}$ )	Surface Area ( $\text{g}/\text{m}^2$ )	Initial pH
Goethite	Fe oxide	$\sim 1$	12.7	2.8
Montmorillonite	2:1 clay	< 5	95.4	8.4
Gibbsite	Al hydroxide	< 2	5.5	8.9
Kaolinite	1:1 clay	< 3	12.0	4.6
Quartz	crystalline	< 53	0.7	6.0

Table 2: Results from sorption isotherm model fitting where  $K_L$  = Langmuir constant,  $C_w$  = aqueous concentration,  $C_s$  = amount adsorbed,  $C_{s,\text{max}}$  = maximum amount adsorbed as  $C_w$  increases,  $K_F$  = Freundlich constant, and  $n$  = correction factor.

pH	Mineral	Langmuir Isotherm			Freundlich Isotherm		
		$C_{s,\text{max}}$ (mg/g)	$K_L$	$R^2$	$n$	$K_F$	$R^2$
4	Goethite	839621.16	0.09	0.94	0.13	389034.08	0.99
6		1101612.14	0.62	0.98	0.04	894938.18	0.99
4	Montmorillonite	416068.19	0.04	0.93	0.22	103606.45	0.87
6		998750.66	0.10	1.00	0.09	567382.64	0.93
4	Gibbsite	455048.3209	0.14	0.61	0.08	277647.07	0.78
6		448762.4929	0.22	0.71	0.06	309762.85	0.87
4	Kaolinite	162604.79	0.03	0.96	0.11	76379.08	0.85
6		253034.28	0.01	0.91	0.07	127997.38	0.68

## 1.0 Introduction

Maintaining soil organic matter (SOM) stocks is crucial to soil fertility, climate mitigation, and increasing agricultural sustainability in a rapidly changing world (Schmidt et al., 2011). Mineral-associated organic matter (MAOM, <53  $\mu\text{m}$ ) is a pool of SOM which has a mean residence time of decades to centuries and has thus gained attention as a reservoir for long-term carbon storage (Lavallee et al., 2019; Sokol et al., 2019; Wiesmeier et al., 2019). While many studies have probed the MAOM pool, the complexity and heterogeneity of soil environments has made it difficult to understand the mechanisms and controls of MAOM accumulation and longevity (Degryze et al., 2004; Cotrufo et al., 2019; Leichty et al., 2020). Therefore, a simplified, model system is needed to parse apart factors in the soil environment impacting organo-mineral interactions contributing to the MAOM pool.

Specifically, past research has identified the importance of mineral properties such as surface area and structure in providing sites for organic matter bonding (Vogel et al., 2015; Ahmat et al., 2019). Surface properties cannot be examined without considering the influence of solution pH in determining the charge of mineral surfaces and organic constituents (Newcomb et al., 2017). Therefore, minerals with a range of properties such as surface area, particle size, and initial pH need to be tested to understand the impact of mineral properties and under different solution pH conditions.

To understand the longevity of mineral associations, researchers have applied a plethora of techniques which subject organo-mineral complexes to different pressures including physical force, thermal energy, and chemical extractions. The application of physical force through techniques such as Dynamic Force Microscopy provides accurate, quantitative information on bonding strength but is time intensive as well as costly (Newcomb et al., 2017). Sequential chemical extractions involve the use of increasing aggressive solvents to isolate SOM fractions of increasing stability. This technique is useful for isolating SOM fractions based on bonding strength can but introduce artifacts when soil constituents are subjected to high temperatures during extraction and are difficult to relate to field-measurable SOM pools (Lopez-Sangil and Rovira, 2013). Lastly, thermal energy can be applied to organo-mineral bonds which can be used as a proxy for bonding strength. A recent study using thermal desorption found that the higher the desorption energy to break organo-mineral bonds, the longer the residence time (Sanderman and Grandy, 2020). Therefore, we will employ a thermal desorption technique, pyrolysis-mass spectrometry/gas chromatography which has been shown to capture organo-mineral binding strength for simple systems when adequate standards are included.

While bonding strength is an important metric for understanding MAOM longevity, it does not provide mechanistic information about the mineral interface. ToF-SIMS analysis provides a molecular view of organo-mineral interactions at the surface of minerals. The understanding of changes in ionic composition at the surface of minerals allow us to probe the adsorption mechanisms at the organo-mineral interface. ToF-SIMS has proven useful for studying soil environments, particularly when paired with principal component analysis (PCA) to consolidate the complexity of interpreting hundreds of resulting peaks (Huang et al., 2021). In this study, we propose the use of Py-GC/MS and ToF-SIMS to quantify bonding strength and uncover interactions at the mineral-organic matter interface .

## 2.0 Materials and methods

This study can be divided into two parts: batch sorption experiments to identify the sorption capacity of biomolecules on each mineral and analyses of the organo-mineral binding strength and identity of post-sorption solids using a ramped thermal technique and ToF-SIMS.

### 2.1 Biomolecule and mineral selection

Biomolecules and minerals were selected for their ubiquitous nature in terrestrial systems. Specifically, tannic acid (TA) was chosen because it is a biomolecule produced in abundance across a wide variety of plants. Quartz was chosen as a mineral control due to its low surface area and largely unreactive surfaces. In order to stay consistent with MAOM-sized ( $<53\text{ }\mu\text{m}$ ) particles, quartz was ground with a mortar and pestle and sieved to isolate fine-sized quartz particles. The other minerals tested came from various mineral classes including Fe oxides (goethite), Al oxides (gibbsite), 1:1 (kaolinite) and 2:1 phyllosilicate (montmorillonite) which are key players in C sorption (Han et al., 2021). All compounds and minerals were used as received and all sourced from Sigma-Aldrich except for Ca-montmorillonite and kaolinite (Clay Mineral Society, Boulder, CO, USA). Mineral surface area was assessed by BET analysis based on N2-gas adsorption (Micromeritics analyzer). Particle size was estimated by scanning electron microscopy (Hitachi, Tokyo, Japan) images obtained after mounting minerals on double-sided tape and coating with 6 nm Iridium (Table 1, Fig. 1).

### 2.2 Batch sorption experiment

Batch sorption experiments were performed by mixing 1.00 g aliquots of minerals with 20 mL of biomolecule solutions in 50 mL glass centrifuge tubes. All glassware was acid washed and sterilized in a muffle oven to ensure the exclusion of microorganisms that could degrade tannic acid. A range of tannic acid solutions were prepared by diluting stock solutions with ultra-pure water to target the following concentrations: 0, 200, 400, 600, 800, 1000, 1200, 1400 mg compound L<sup>-1</sup>. 10 mM of NaCl solution was added to each tube to control for the effect of increasing compound concentrations on solution conductivity. Each sorption experiment included a biomolecule control without mineral presence (1400 mg compound L<sup>-1</sup>), and a mineral control without biomolecule presence. To control and explore for the effect of pH, solutions were corrected to pH 4 and 6 using dilute HCl and NaOH solutions. Concentrations were tested in triplicate except for controls; thus, a batch consisted of 26 tubes shaken for 48 h on a reciprocal shaker (150 rpm). After 24 h, solution pH was measured and corrected to  $\pm 0.1$  units from the pH of interest (4 or 6). Samples were harvested after 48 h by measuring and recording the solution pH, centrifuging at 4000 rpm for 20 minutes and filtering the solution through a pre-rinsed 0.22  $\mu\text{m}$  filter (Fisher, Hampton, NH, USA). Compounds left in solution were quantified by UV-vis spectrophotometry at 295 nm for tannic acid.

The quantity of TA sorbed to a mineral was calculated by the difference in concentration between the amount added and the amount measured in solution post-sorption. The relationship between TA quantity and plate reader absorbance was established by fitting a linear trend line to a standard curve of six known TA concentrations. Sorption isotherms exhibited asymptotic relationships with increasing starting concentrations; therefore, linear Langmuir and Freundlich curves were fit to approximate bonding mechanisms. Briefly, Langmuir model assumed a monolayer of organic molecules adsorbed to singular sites on the adsorbent surface. Freundlich model considers multi-layer bonding through surface heterogeneities and organo-organo interactions. Model fits were compared using R<sup>2</sup> values.

The Langmuir equation is expressed here as:

$$\frac{1}{C_s} = \left( \frac{1}{C_{s,max} * K_L} \right) \frac{1}{C_w} + \frac{1}{C_{s,max}} \quad (\text{eq. 1})$$

where  $K_L$  = Langmuir constant,  $C_w$  = aqueous concentration,  $C_s$  = amount adsorbed,  $C_{s,max}$  = maximum amount adsorbed as  $C_w$  increases.

The Freundlich equation is expressed here as:

$$\log C_s = n \log C_w + \log K_F \quad (\text{eq. 2})$$

where  $K_F$  = Freundlich constant,  $n$  = correction factor,  $C_w$  = aqueous concentration,  $C_s$  = amount adsorbed.

### 2.3 Evolved gas analysis

Sorption solids were dried at 50°C, ground using a mortar and pestle, funneled into quartz tubes (CDS Analytical Inc., Oxford, PA, USA), and packed with glass wool. Pyrolysis–GC/MS analyses were performed using a CDS 6200 series pyrolyzer with an attached autosampler (CDS Analytical Inc., Oxford, PA, USA) joined to a Shimadzu GCMS-QP2020NX (Shimadzu Corporation, Kyoto, Japan). Evolved gas analysis (EGA) was used to determine temperature ranges for distinct thermal fractions by exposing the samples to a 20°C min-1 temperature ramp from 100 to 700°C. Evolved gasses were processed through a 1-meter steel transfer line maintained at an isothermal (300°C) with a back pressure setting of 87 psi to the GC inlet. Once sample entered the GC inlet the gasses were fractionated at a split ratio of 15:1 to prevent overloading and sent directly to the mass analyzer at 1 mL min-1 using a length of deactivated capillary 5m x 0.25mmID (Restek, Bellefonte, PA, USA) as proxy for a separation column. The GC oven was maintained at a transfer line matching isothermal (300°C).

### 2.4 ToF-SIMS analysis

GT-TA sorption solids were used for ToF-SIMS analysis to characterize the change in surface ions with increasing TA sorption and different solution pH (4 and 6). Samples were prepared similarly to Huang et al., 2021. Briefly, a few milligrams of powdered sorption solid were pressed into indium foil to ensure a flat surface for analysis by a TOF.SIMS5 instrument (IONTOF GmbH, Münster, Germany). Samples were pre-treated with a low-energy (10 eV) electron flood gun to compensate for sample charging. SIMS spectra was collected using a 25 keV pulsed Bi<sup>+</sup> beam with a current of 0.54 pA. The beam was focused to a spot ~5 μm in diameter and scanned over a 200 × 200 μm<sup>2</sup> area with a data collection time of roughly 100 s for each spectrum. Six positive ion spectra and six negative ion spectra were collected at different locations for each sample. PCA analysis of unit mass spectra were performed with Python, generating plots which distinguish samples and provide chemical speciation information.

## 3.0 Results and discussion

### 3.1 Organo-mineral loading rates

It is important to note that our isotherm experiment excluded biogenic interactions by microorganisms which have been shown to both enhance and diminish soil organic matter stocks depending on the physiological characteristics and life strategies of the microbial community (Creamer et al., 2019). In order to limit the number of experimental variables and thus the complexity of the system, we focused on abiotic sorption dynamics. The amount of TA sorbed onto the five minerals differed significantly based on mineral identity and solution pH. Mineral surfaces saturated at different concentrations of TA with quartz (QZ) saturating at ~50 ppm, kaolinite (KE) at ~175 ppm, gibbsite (GB) at ~450 ppm, montmorillonite (MT) at ~450 ppm at pH 4 and ~950 ppm at pH 6, and goethite (GT) at ~1000 ppm (Fig. 1).

When considering the physical properties of the minerals, it was not surprising that QZ and KE did not sorb much TA due to low surface area which has been shown in previous studies (Rakhsh et al., 2020). In contrast, it was surprising that goethite sorbed more TA than MT, since MT has a much higher surface area (Table 1). Looking more closely at these two minerals, the surface charge of MT was severely changed by the significant lowering of solution pH by HCl addition. Past research showed decreased basal site density when acid was added to MT due to the dissolution of SiOH groups (Jeon and Nam, 2019). Therefore, solution pH was a driving factor in determining MT sorption capacity by altering bonding sites available for tannic acid. The other minerals tested did not exhibit a strong difference in sorption capacity except for a small increase in sorption for goethite at pH 6. This increase might stem from a change in GT structure to hematite (Schwertmann and Murad, 1983), which has been shown to preferentially sorb aromatic compounds (Adhikari and Yang, 2015).

Isotherm data is not only useful for determining the quantity of a compound sorbed to a mineral but can be fit to isotherm models to give insight into bonding organization such as monolayer or multilayer sorption. Isotherm data was fit to Langmuir and Freundlich equations, except for quartz which did not fit either model well due to low TA sorption (Table 2). The GB-TA isotherm did not fit very well with either model due to an uptick in sorption at the highest initial TA concentration. This uptick could be the results of human error in setting up the isotherm or slight bias when diluting the isotherm solution before being run on the plate reader. If the final concentration was removed from the model fit, the Langmuir model would have a much better fit as evidenced by the clear L-shaped curve of the dataset. The GT-TA isotherm data was fit best by a linear Freundlich equation which suggests multi-layer, non-homogenous bonding while the other minerals were better described by Langmuir which suggests monolayer bonding.

### 3.2 Mineral identity but not solution pH impacted bonding strength

Pyrolysis evolved gas analyses revealed differences between the thermal sensitivity of free versus adsorbed compounds and demonstrated that pH affected the amount of biomolecules adsorbed on mineral surfaces. Meanwhile, mineralogy and the type of organic compound affected the quantity and strength of biomolecule adsorption. Thermal stability of biomolecules was enhanced after interactions with minerals, through different mechanisms such as Ca ion complexation, adsorption, and/or coprecipitation. EGA

spectra at pH 4 and 6 are identical for adsorbed TA to both minerals (Fig. 3). It suggests that pH had no effect on sorption strength of TA to both minerals, although the quantity of TA adsorption was regulated by pH. This finding is contradictory to other studies which denoted stronger bonding at low pH due to inner-sphere coordination (Kleber et al., 2005; Newcomb et al., 2017). Perhaps if we had tested a wider range of pH which included basic soils, we would have observed this trend, but we chose to focus on pH values that are more commonly seen within field situations.

The evolved gas peak of TA adsorbed to MT at pH 6 shifted to a higher temperature, compared with TA control without adsorption to MT (Fig. 3) likely from the presence of Ca ions which are known to stabilize OM compounds (Rowley et al., 2018). EGA peak of TA with exposure to MT at pH 4 was at the same temperature as TA control at pH 4. Evolved gas peaks of TA adsorbed to GT had higher temperature than peaks of TA controls at both pH 4 and 6. TA adsorbed to GT was evolved at multiple temperatures during pyrolysis treatment, indicating potential layering adsorption of TA to GT which is supported by our modeling fitting results presented in section 3.1.

### 3.3 ToF-SIMS revealed preferential sorption of tannic acid at higher aqueous concentrations

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) determined that the ionic composition of goethite surface changed with increasing concentrations of TA that adsorbed to goethite. We found that goethite (GT) surface ions, such as  $\text{Fe}^+$ ,  $\text{Fe-O}$  clusters, substituted  $\text{Al}^+$  and  $\text{K}^+$ , were covered by TA related ions with increasing concentrations of adsorbed TA (Fig. 4). Chlorine and sulfate ions at the surface of GT were replaced by sodium-containing TA related ions along with increasing concentrations of adsorbed TA (Fig. 4). In addition, pH also altered surface ionic composition of TA-goethite complexes by increasing sodium ions at a higher pH (Fig. 4). Thus, both adsorbed TA concentration at the GT surface and pH affect the ionic composition at the mineral surface, reflecting the binding mechanisms at the organo-mineral interface. Although not as effective as  $\text{Ca}^{2+}$ , sodium cations can act as a bridge between organic matter functional groups and mineral surfaces, forming outer-sphere complexes (Galicia-Andrés et al., 2021). Therefore, as bonding sites on GT became more favorable for sodium ions as pH increased, more TA constituents were able to bond and create multi-layer organo-organo interactions as outlined within what is colloquially known as the “Onion Model” (Kleber et al., 2007). This finding of multi-layer sorption is supported by our modeling and EGA results which shows the power of multiple lines of evidence and the complementarity of these diverse data streams.

## 4.0 Conclusions

The sorption isotherms and subsequent Py-GC/MS and ToF-SIMS analyses revealed differences in bonding strength and surface ions at the mineral-organic matter interface. From the set of data, it appears that the common polyphenol, tannic acid, is mainly adsorbed to mineral surfaces in a monolayer except for multi-layer bonding seen on the iron oxide, goethite. This multi-layer bonding increased the sorption capacity of goethite and increased the thermal stability of tannic acid. ToF-SIMS provided insight into the potential mechanisms at play at the mineral interface, likely sodium ion bridging between negatively charged sites and negative OM functional groups. We recommend continued research utilizing these previously siloed techniques to uncover molecular-scale information about organo-mineral bonding. The information gained from these techniques will be essential in developing our understanding of factors impacting the formation of MAOM which is an important SOM pool.

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