ENERGY OF AMINO-BEARING ORGANIC MOLECULES AT THE FERRIHYDRITE-WATER INTERFACE

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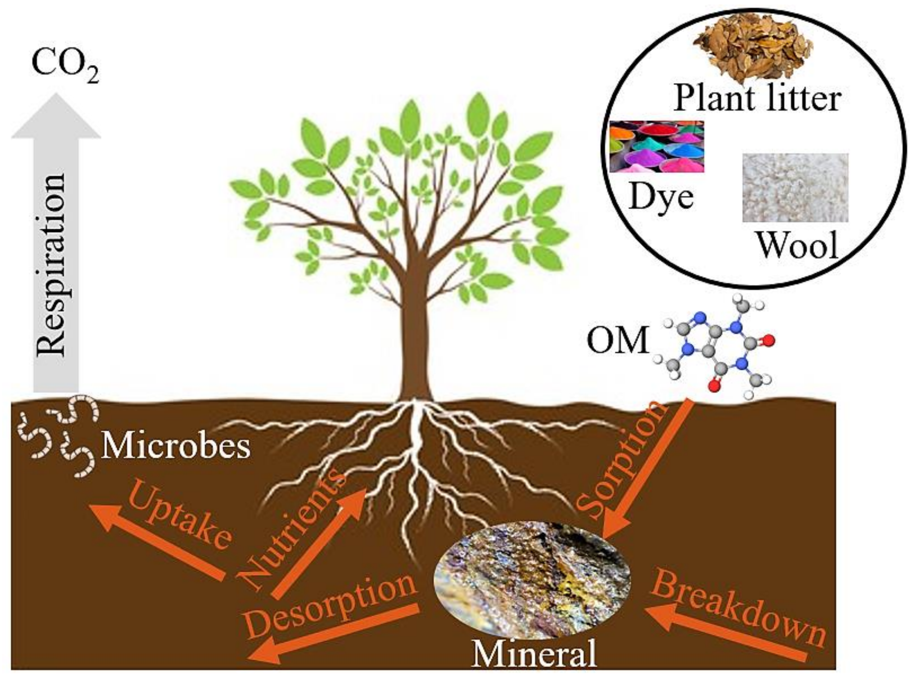
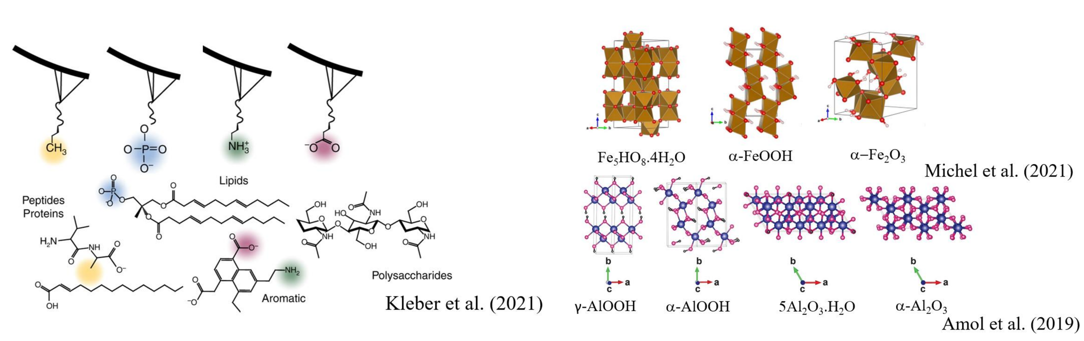
Introduction

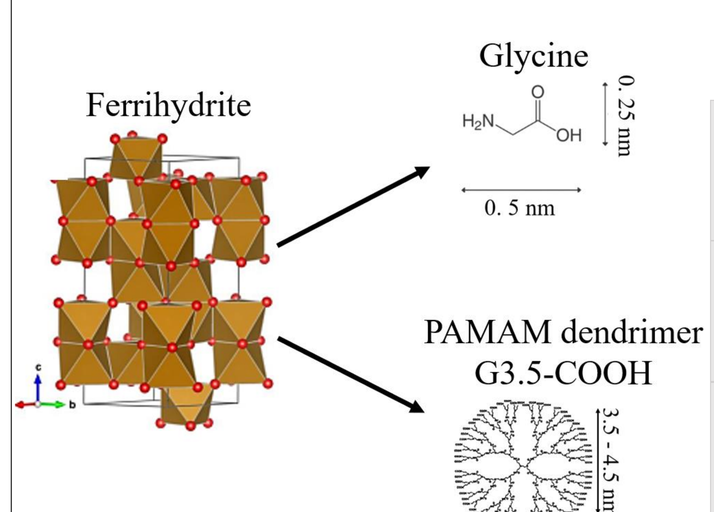
ORGANIC MATTER (OM)-MINERAL INTERACTIONS IN THE ENVIRONMENT



COMPLEXITY IN OM-MINERAL SYSTEMS



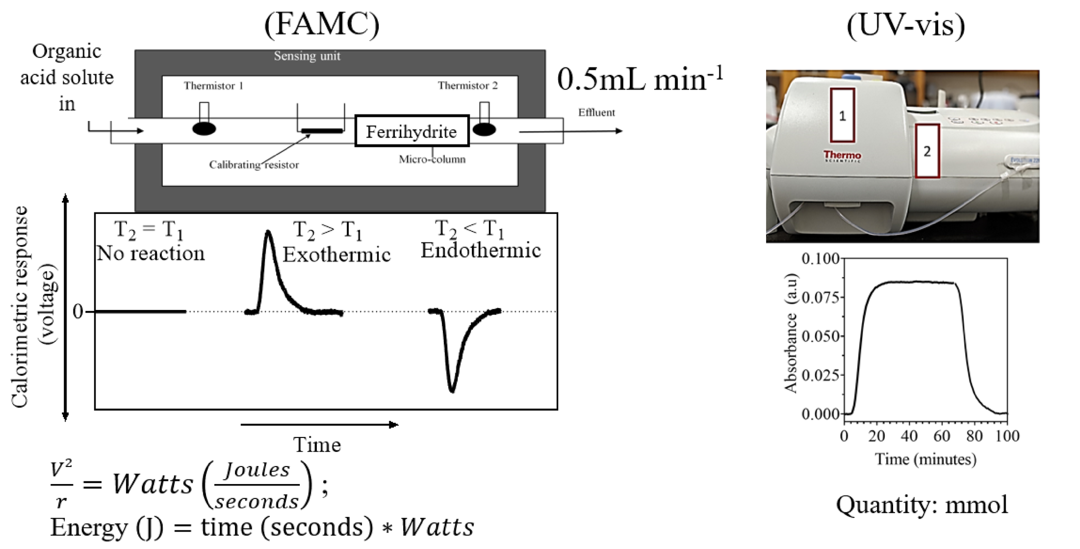
MATERIALS & OBJECTIVES



- At pH 2: ferrihydrite is 100% positively charged; glycine & G3.5-COOH are 96% and 100% cations respectively
- At pH 5: ferrihydrite is 99% positively charged; glycine & G3.5-COOH are100% and 76% zwitterions respectively
- At pH 11: ferrihydrite is 1% positively charged; glycine & G3.5-COOH are both 100% anions

METHODS

FLOW ADSORPTION MICROCALORIMETRY (FAMC) & ULTRAVIOLET-VISIBLE SPECTROSCOPY (UV-vis)

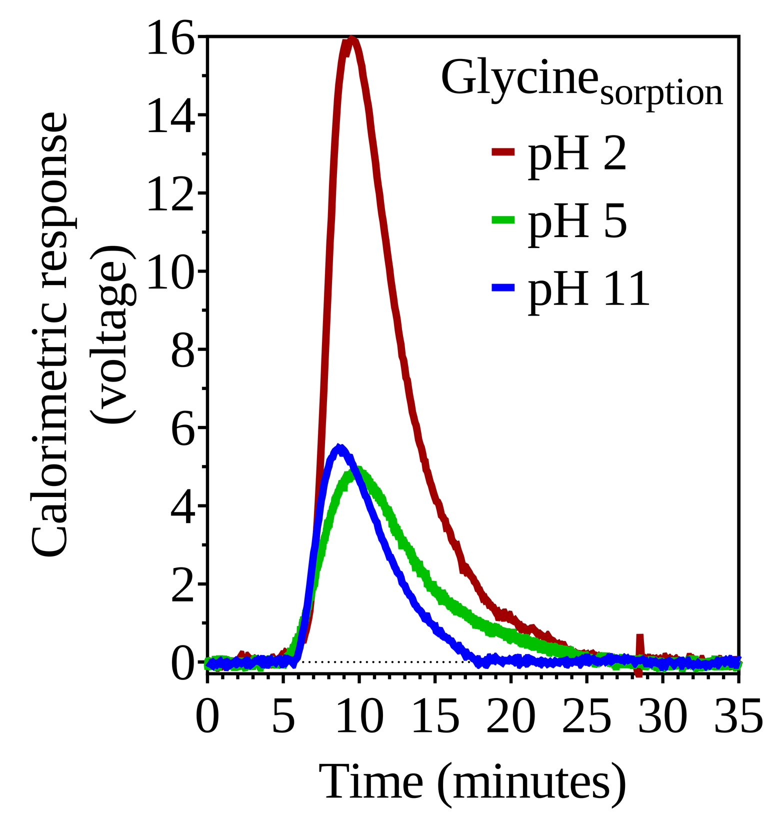


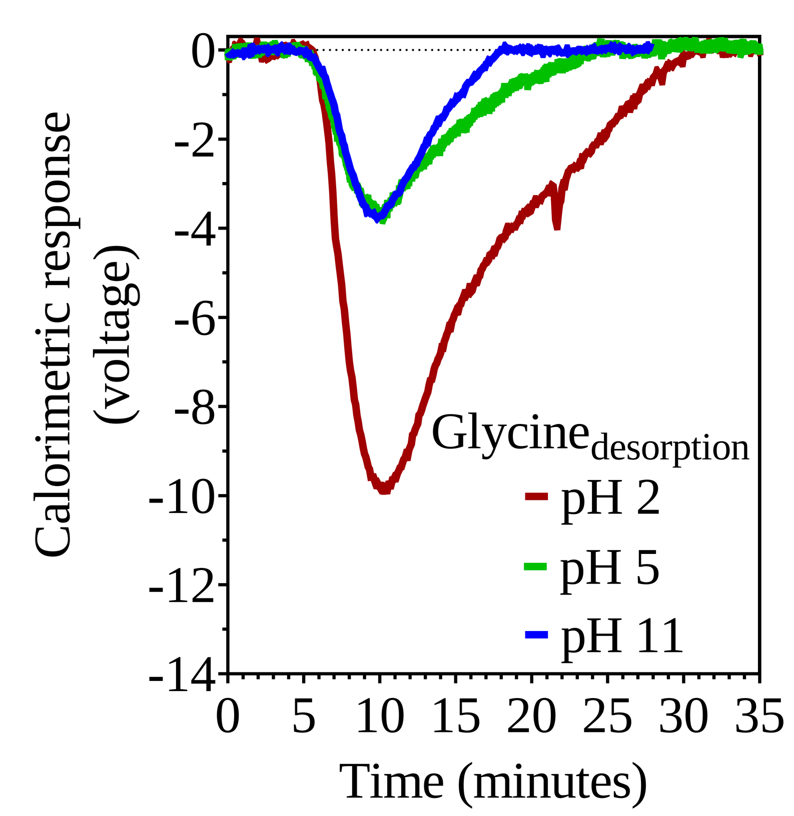
1.Sorption and desorption dynamics, kinetics, and energetics of organic acids on ferrihydrite at pH 2& 5

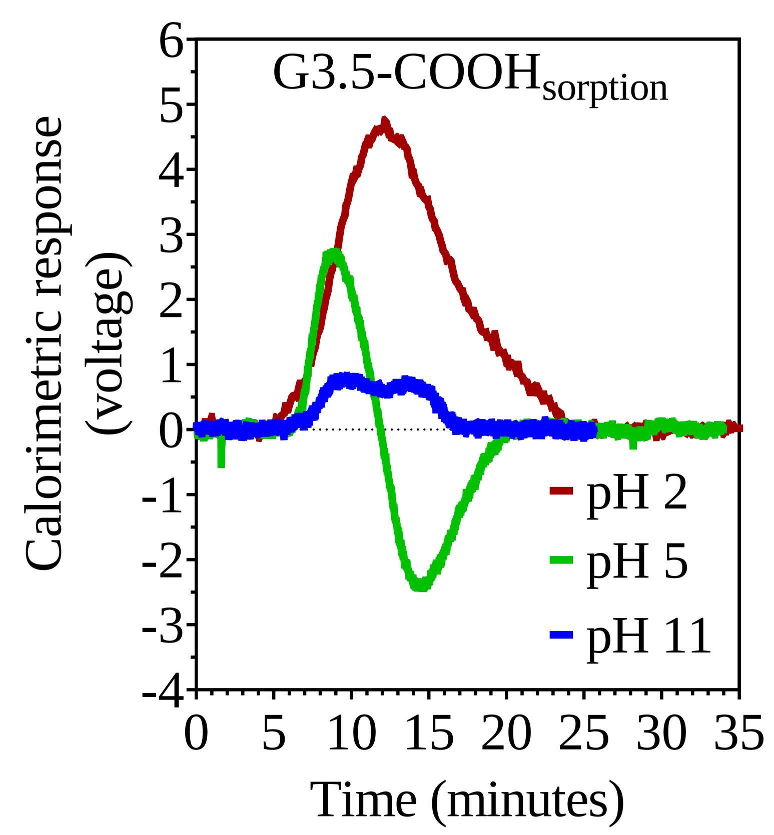
2.Effect on ferrihydrite's surface charge

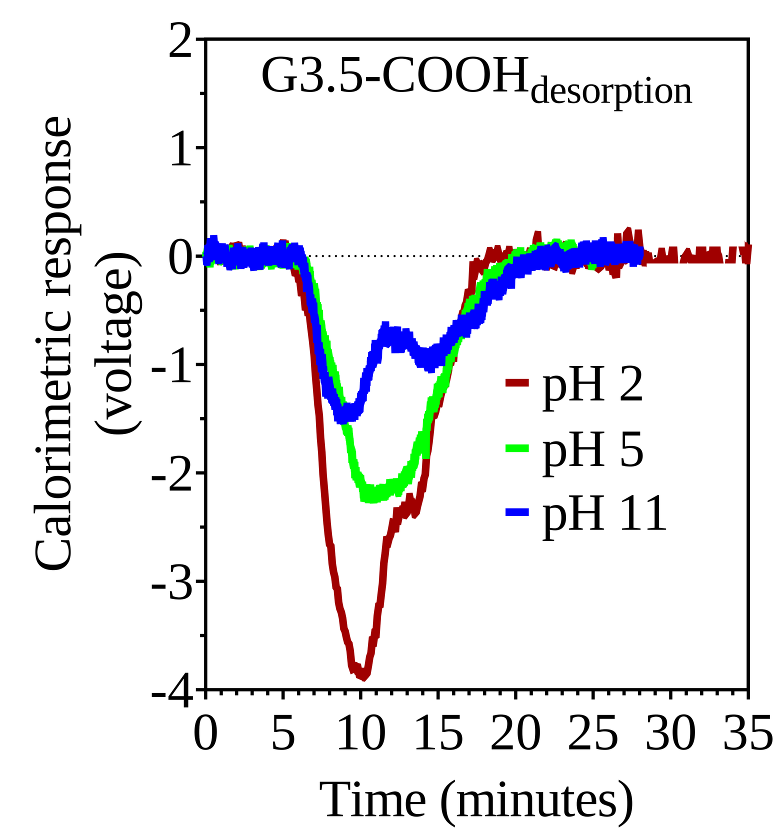
Research Findings

1. SORPTION & DESORPTION DYNAMICS







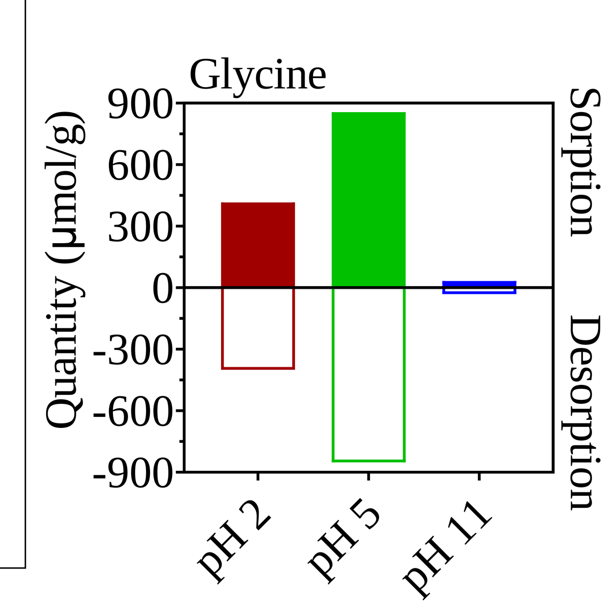


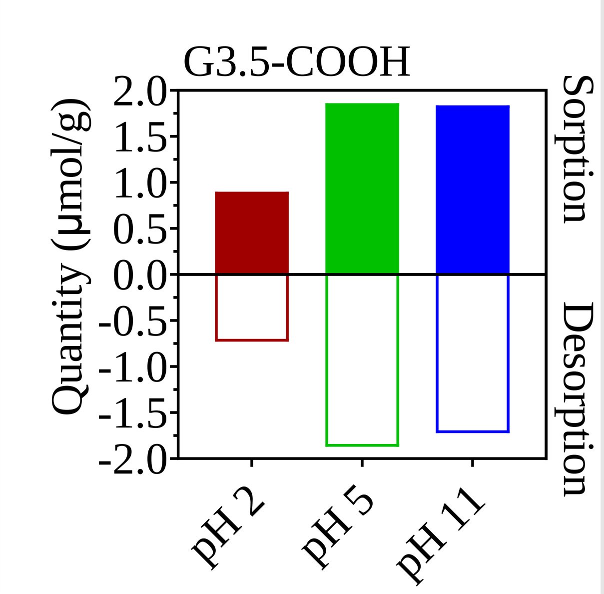
- Across pH glycine sorbs in exothermic reactions
  - decreasing reaction time with pH
- Across pH glycine desorbs in endothermic reactions
  - decreasing reaction time with pH
- At pH 2 G3.5-COOH sorbs in an exothermic reaction
- At pH 5 G3.5-COOH sorbs in mixed reactions (exothermic and endothermic)
- At pH 11 G3.5-COOH sorbs in bimodal exothermic reactions
- Across pH desorption reactions are exothermic
  - bimodal at pH 2 & pH 11

2. QUANTITY, KINETICS & BOND STRENGTH

		Glycine			
		Sorption		Desorption	
		Rxn 1	Rxn 2	Rxn 1	Rxn 2
Reaction rate constant, k' (min^{-1})					
	pH 2	0.47	0.21	0.32	0.15
	pH 5	0.38	0.22	0.33	0.20
	pH 11	0.32	-	0.29	-
Heat of reaction, ΔH (kJ/mol of COO^-)					
	pH 2	18.2	22.3	15.6	41.9
	pH 5	2.6	9.3	2.6	4.5
	pH 11	72.2	-	51.3	-

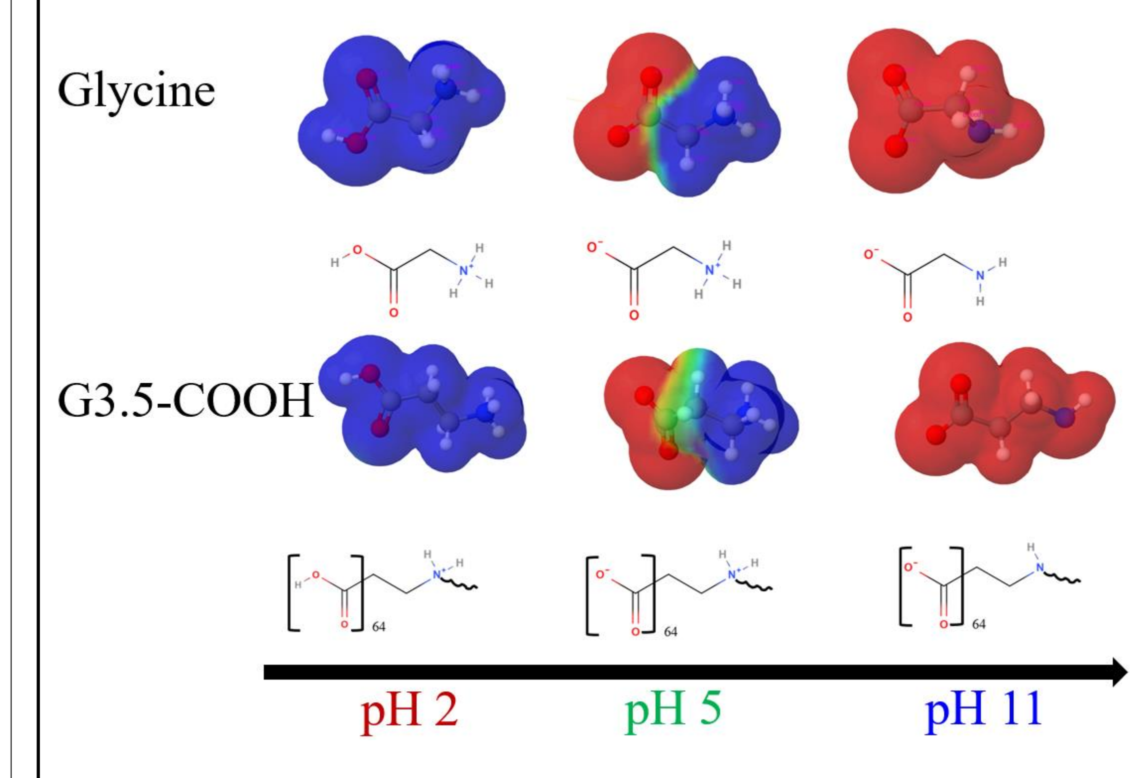
		G 3.5-COOH			
		Sorption		Desorption	
		Rxn 1	Rxn 2	Rxn 1	Rxn 2
Reaction rate constant, k' (min^{-1})					
	pH 2	0.32	0.21	0.53	0.34
	pH 5	0.63	0.27	0.43	-
	pH 11	0.26	-	0.56	0.27
Heat of reaction, ΔH (kJ/mol of COO^-)					
	pH 2	51.0	74.8	33.0	65.0
	pH 5	13.4	22.4	14.1	-
	pH 11	4.1	-	5.3	15.9





- Alkaline pH conditions resulted in fewer reaction steps
- Acidic conditions promoted faster reactions than alkaline conditions
- Previously sorbed molecules were reversible across pH
- Glycine promoted more sorption than G3.5-COOH
- Glycine's strongest bonds are formed in alkaline pH conditions
- G3.5-COOH's strongest bonds are formed in acidic pH conditions

Research findings (continued)



- At pH 2: glycine and G3.5-COOH form non-electrostatic bonds via the unprotonated COOH with the protonated NH_3^+ pointed away from the positively charged ferrihydrite surface
- At pH 5: glycine and G3.5-COOH form electrostatic bonds with ferrihydrite via the deprotonated COO^- with the protonated NH_3^+ pointed away from the positively charged ferrihydrite surface
- At pH 11: glycine and G3.5-COOH form non-electrostatic bonds with ferrihydrite via deprotonated COO^- and NH_2 with the ferrihydrite's surface that is 1% positively charged

Ongoing Work

- Using hematite as the mineral surface to understand the effect of crystallinity on these interactions
- Conduct the experiments at other pH conditions to obtain a gradual understanding of the effect of pH on OM-mineral interactions as a function of pH

Acknowledgements

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References

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- Harvey et. al. (2018), Environmental Science & Technology 2018 52 (11), 6167-6176