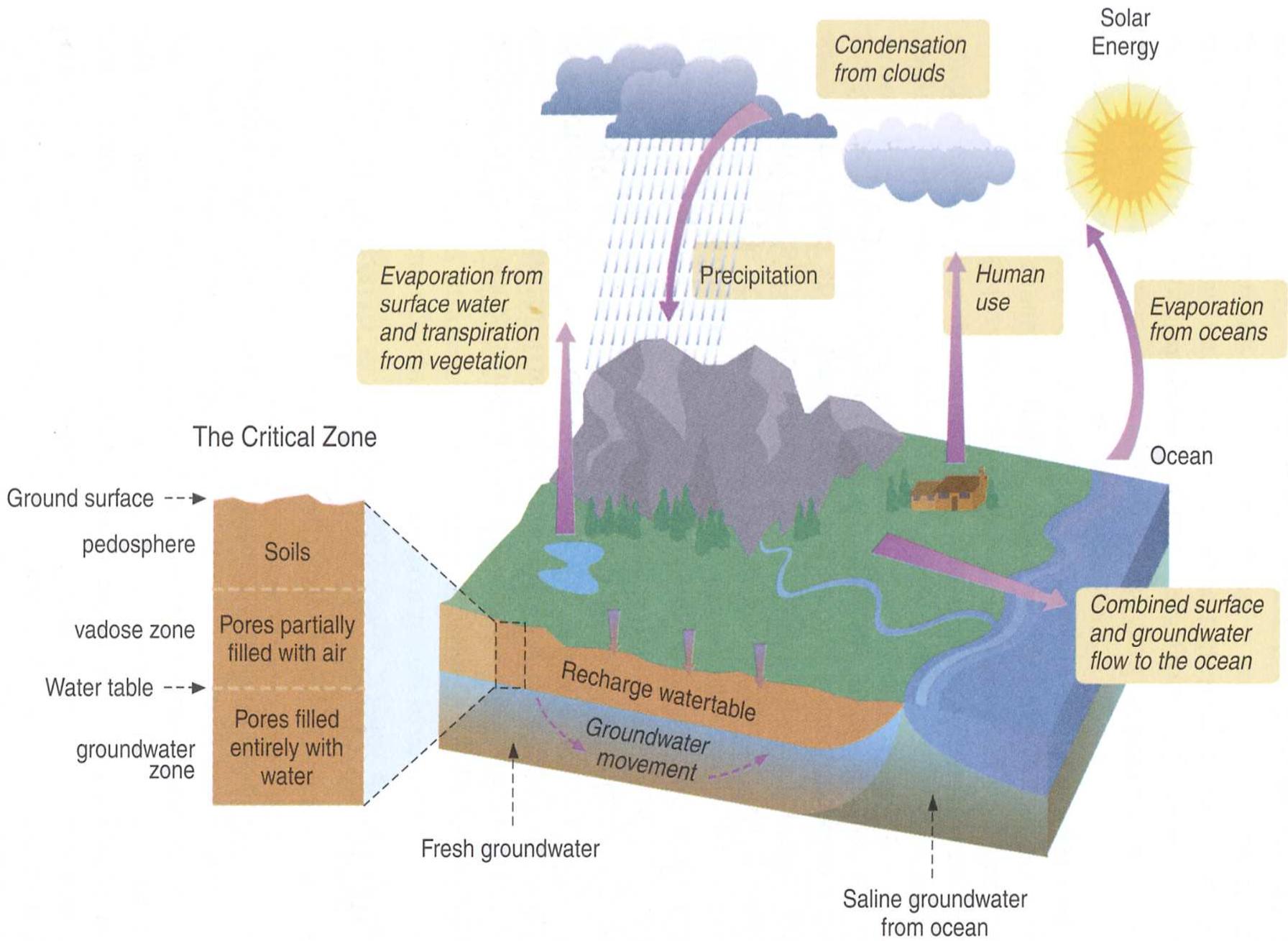


Carbon-Mineral Complexation and Its Role on Carbon Cycling and Sequestration

XXIV Brazilian Congress of Soil Science
Florianopolis, Santa Catalina, Brazil
July 25-August 2, 2013



Donald L. Sparks and C. Chen
University of Delaware



Coupled Process Dynamics Across Spatial and Temporal Scales

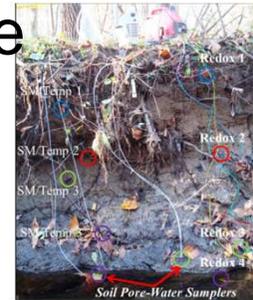
Basin



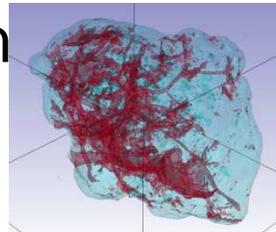
Watershed



Soil profile

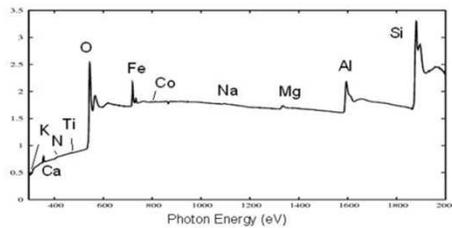


Grain



Molecular

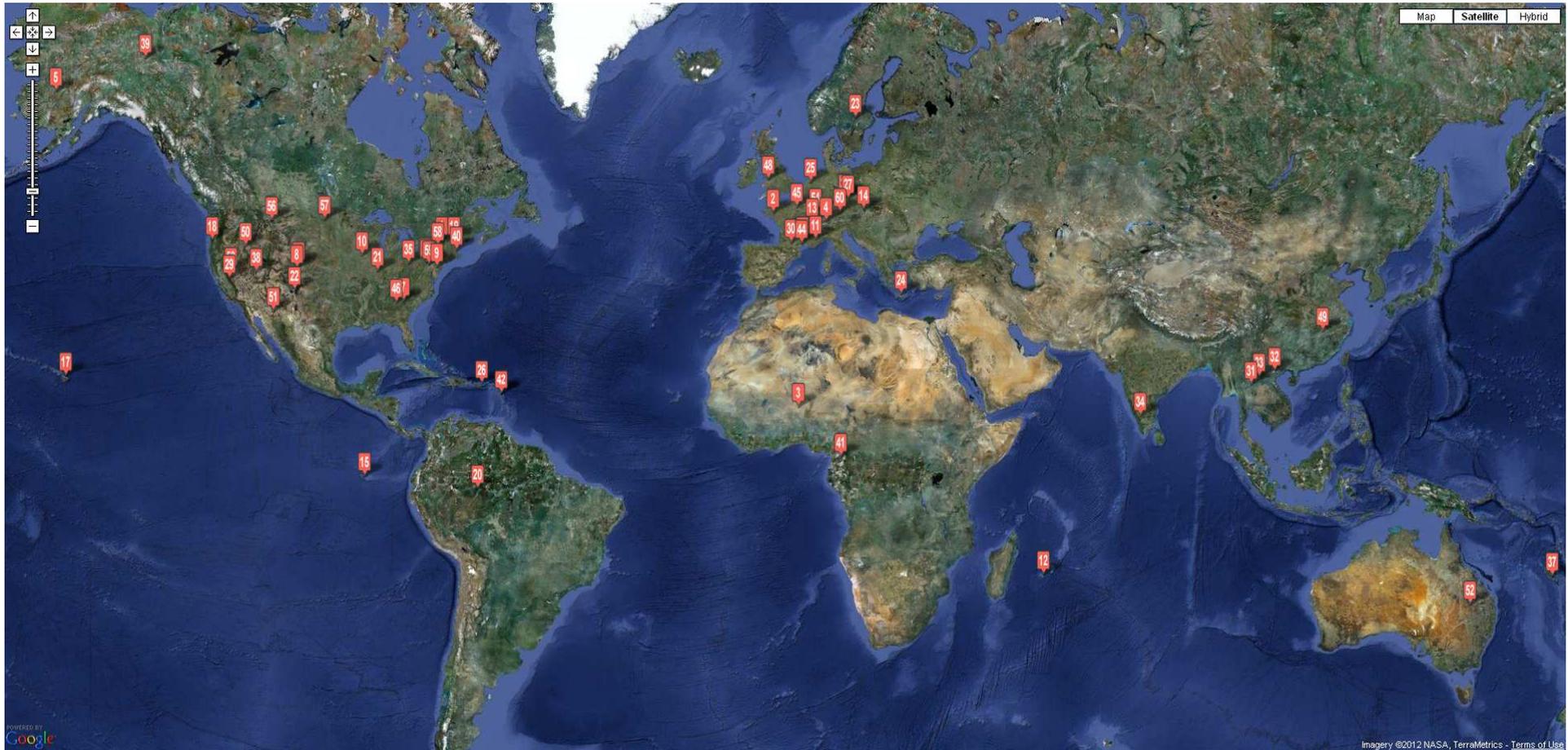
Near-edge X-ray Absorption Fine Structure (NEXAFS)





The Global Laboratory

November 2011 U. Delaware Workshop



Banwart et al. (2012). Sustaining Earth's Critical Zone. Report of the International CZO Workshop, 9-11 November, 2011, U. Delaware. Available from www.soiltrec.eu

CZO Locations



The Christiana River Basin (~1440 km²)

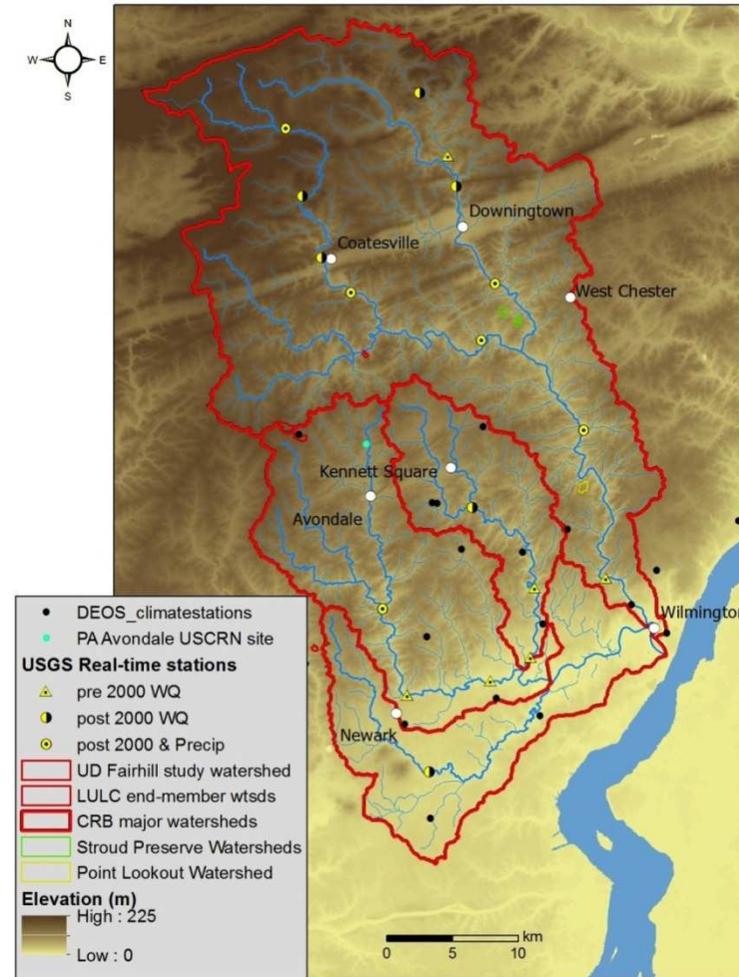
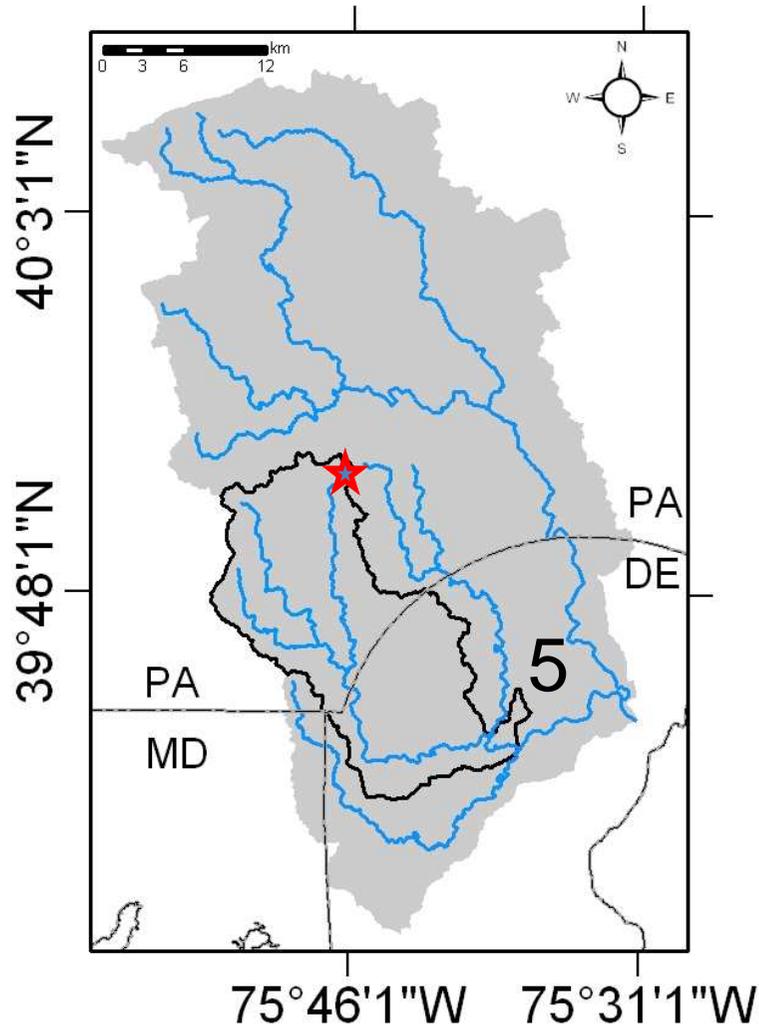
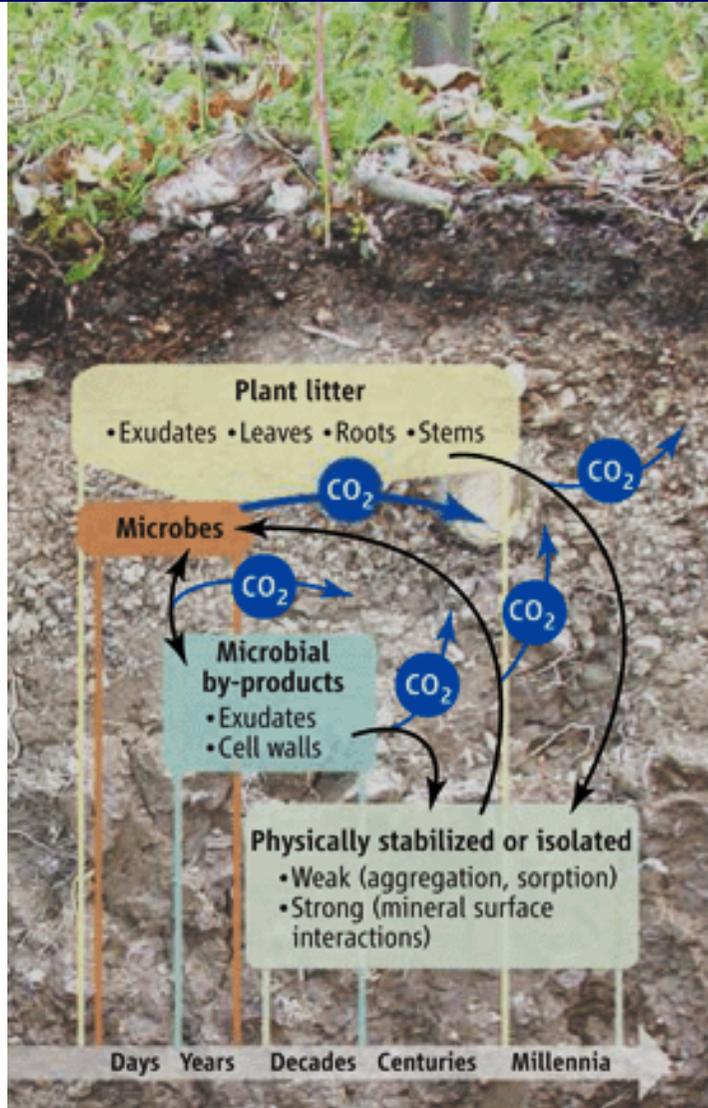


Table 1. Estimated mass of carbon in the world's soils.

SOURCE: USDA.

Soil orders	Area	Organic C
	10 ³ km ²	Gt
Alfisols	13,159	90.8
Andisols	975	29.8
Aridisols	15,464	54.1
Entisols	23,432	232.0
Gelisols	11,869	237.5
Histosols	1,526	312.1
Inceptisols	19,854	323.6
Mollisols	9,161	120.0
Oxisols	9,811	99.1
Spodosols	4,596	67.1
Ultisols	10,550	98.1
Vertisols	3,160	18.3
Other soils	7,110	17.1
TOTALS	130,667	1,699.6

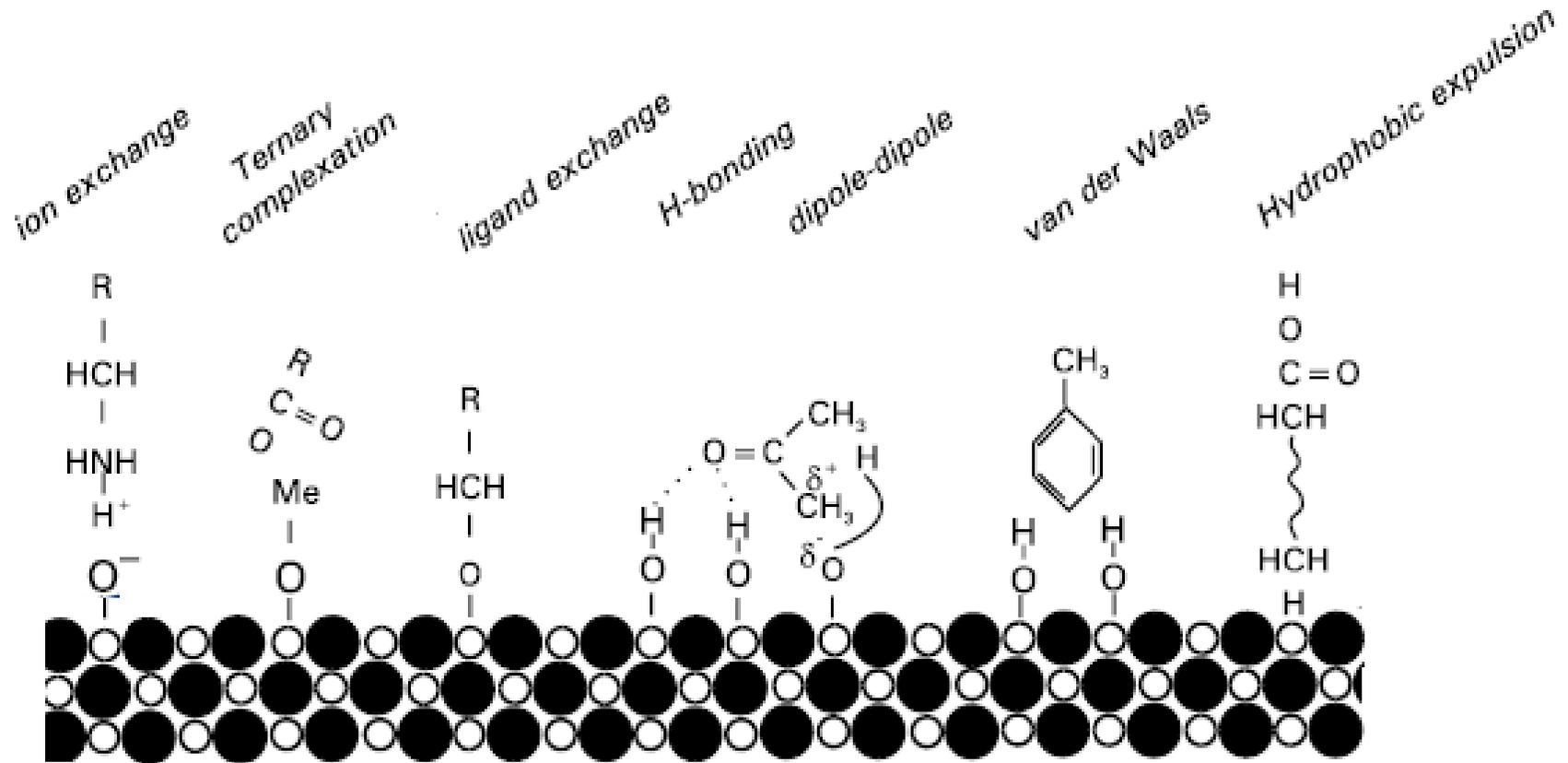
Organo - Mineral Interactions



Adapted from Trumbore et al., 2008

- One of the major mechanisms for C stabilization
- Controlled by the chemistry of organic matter and mineralogy (Fe, Mn and Al oxides, aluminosilicates)

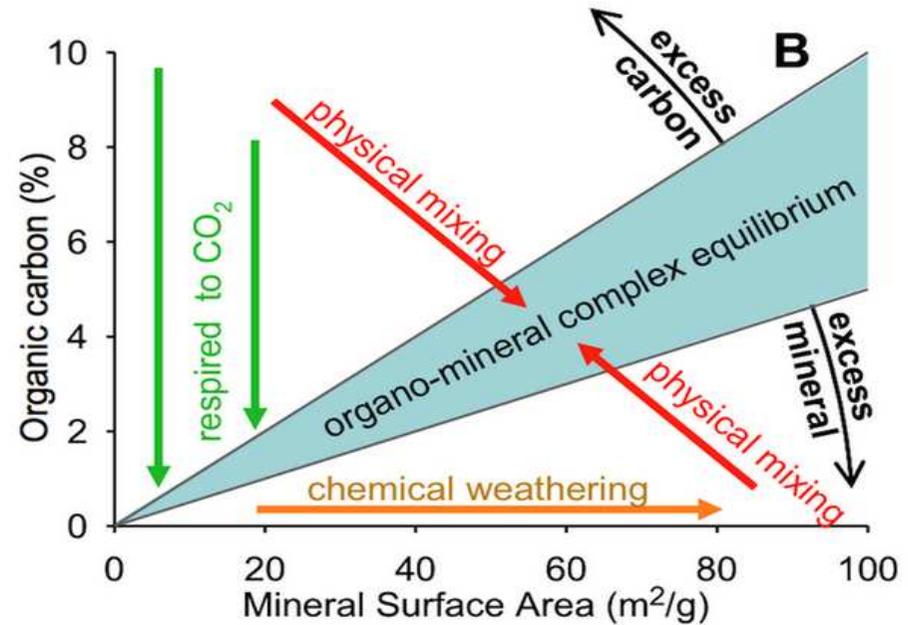
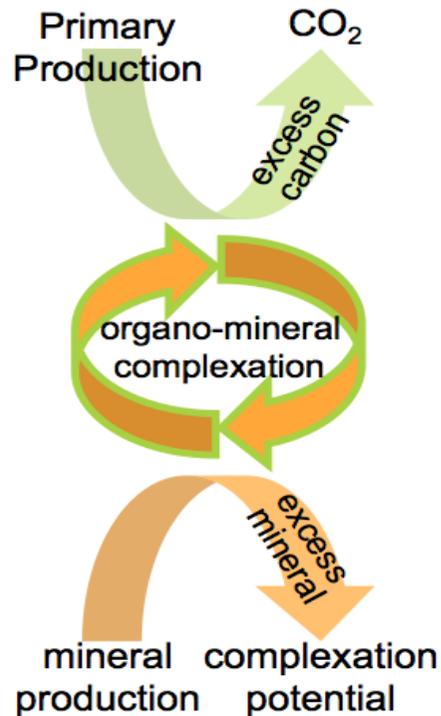
Organic Matter – Mineral Interaction Mechanisms



What are the major mechanisms for organic matter-mineral complexation?

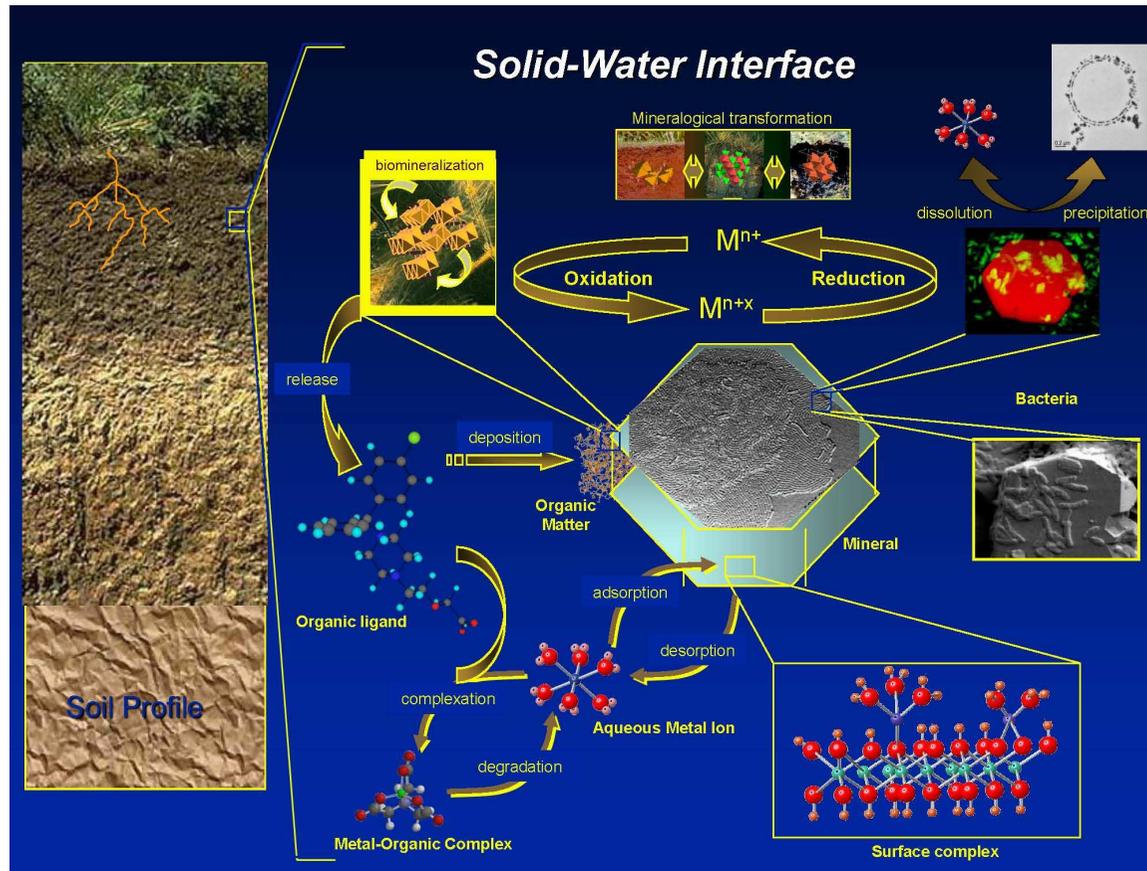


Overall Hypothesis: Organo-mineral complexation, a key process for stabilizing carbon, is limited by the supply of the mineral surfaces and the mixing of minerals with organic matter in natural ecosystems

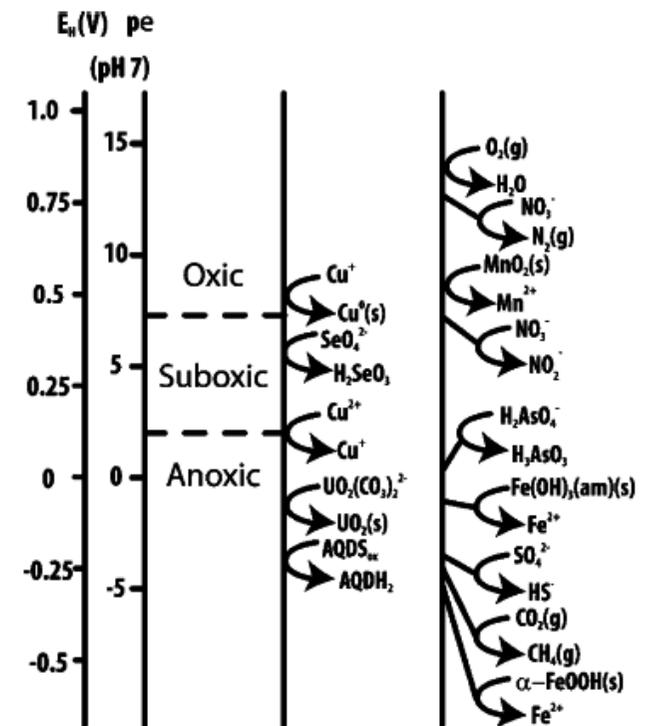


Adapted from www.udel.edu/czo/research.html

Motivation

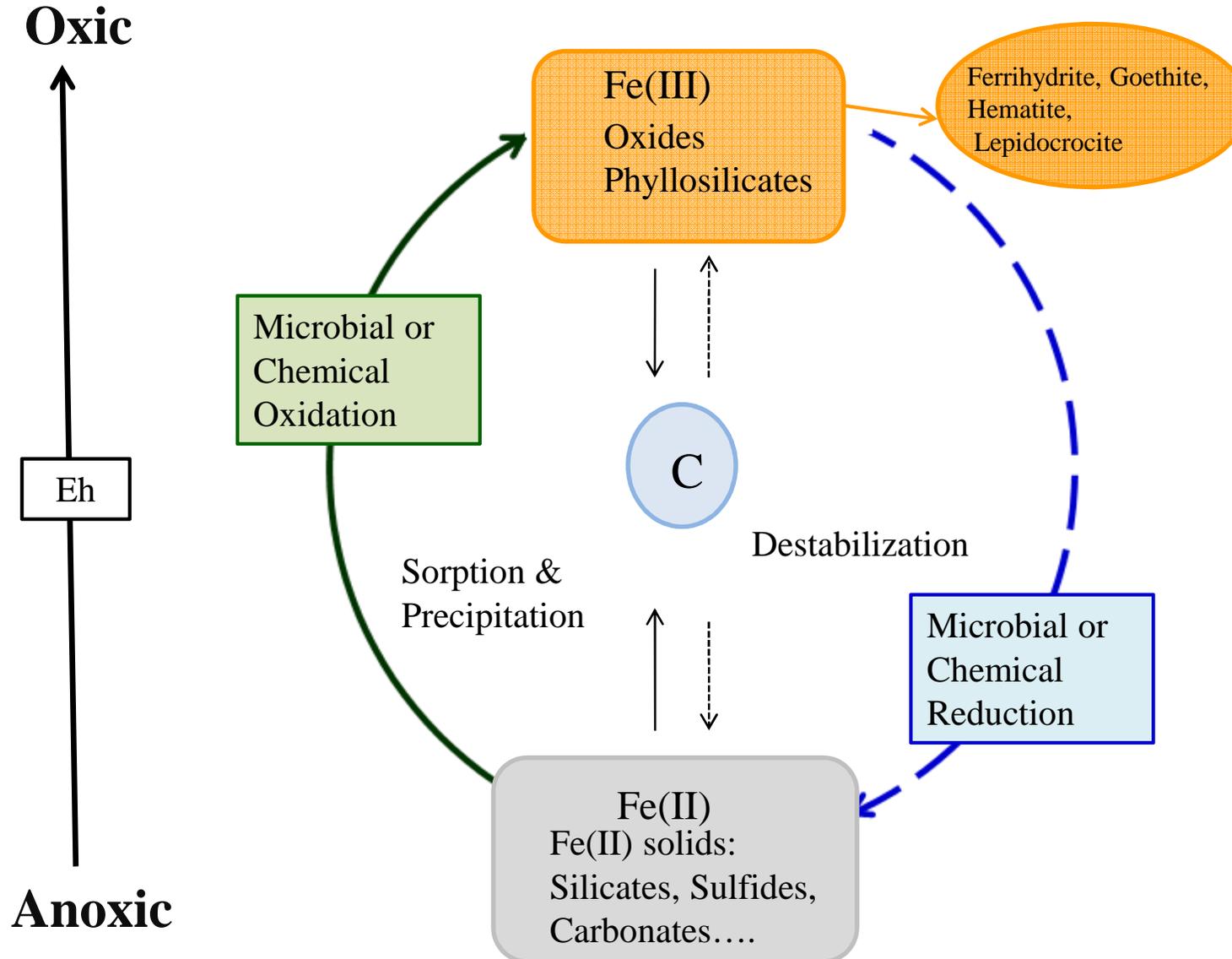


Redox Ladder of Environmentally Relevant Redox Couples



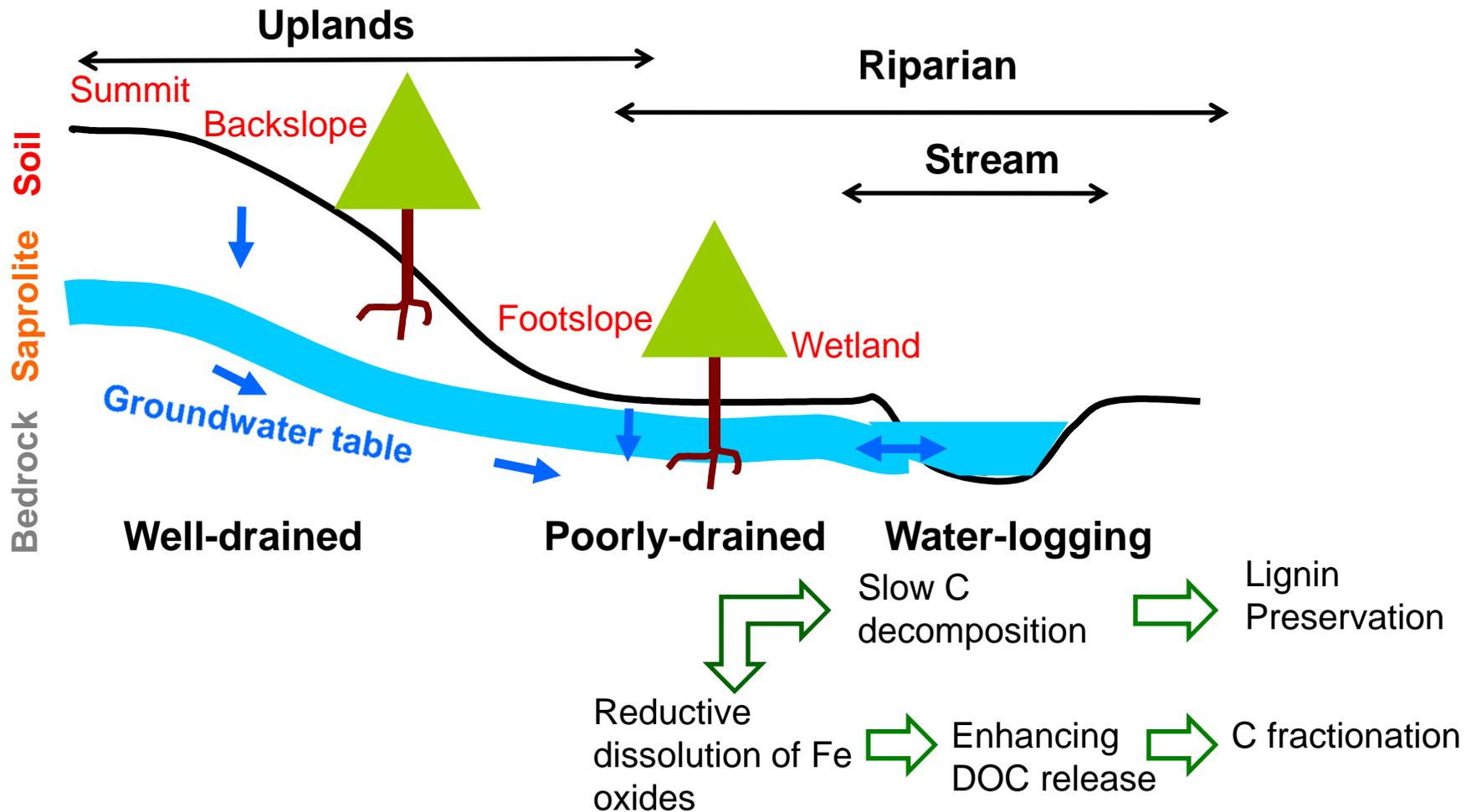
Adapted from Borch et al., 2010; Fendorf et al., 2010

Motivation



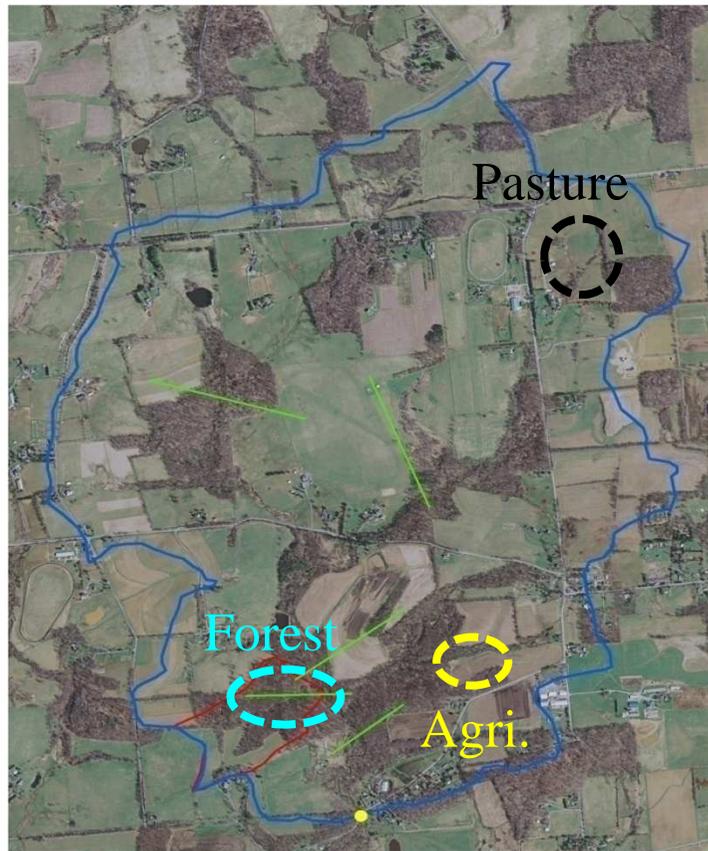
Research Objectives

- **Investigate soil organic matter molecular composition under varying landscape topographic positions**
- **Assess the interactions of C and C forms with soil minerals at the molecular scale**
- **Characterize Fe speciation along the redox gradients**



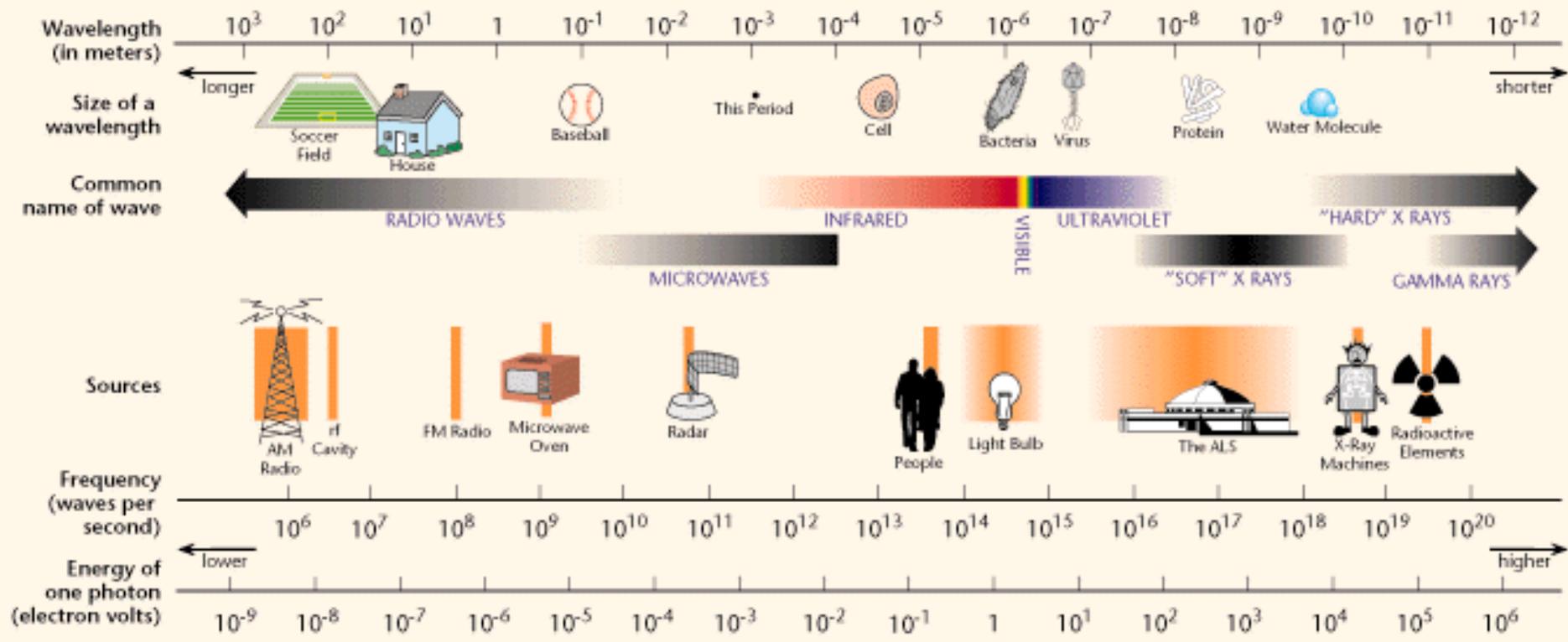
- C and Fe speciation varies along landscape topographic gradients.
- Compared to oxic upland soils, Fe oxides become less important in controlling C sequestration at suboxic-anoxic depositional positions and in wetlands.

Field Sampling



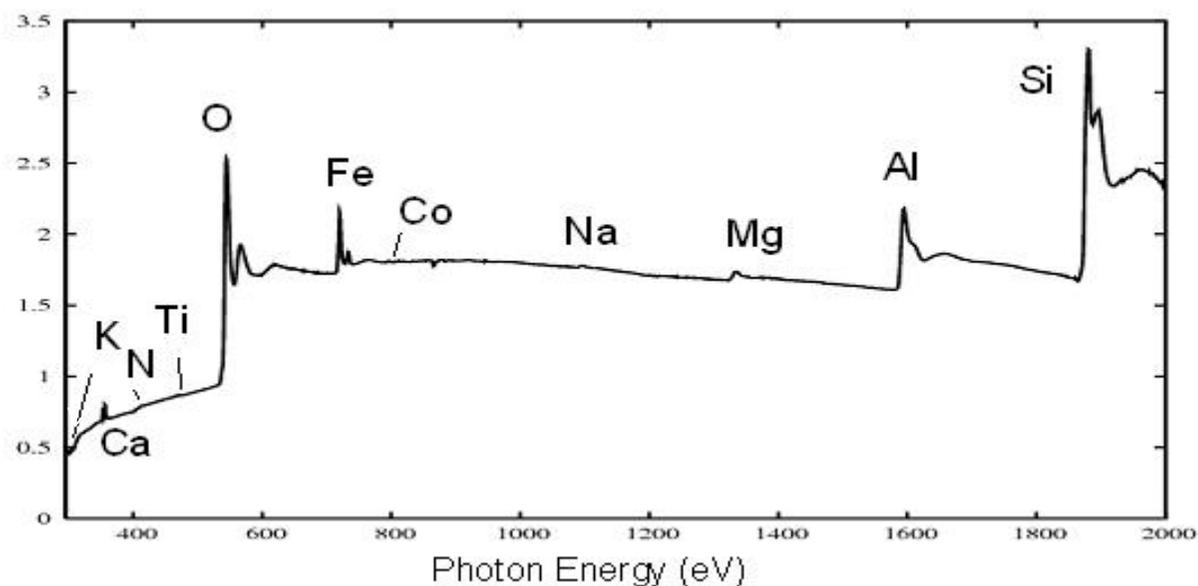
- Pasture, forest, and agricultural hillslopes
- Summit, backslope, and footslope

THE ELECTROMAGNETIC SPECTRUM



Advanced Characterization Techniques

Near-edge X-ray Absorption Fine Structure (NEXAFS)



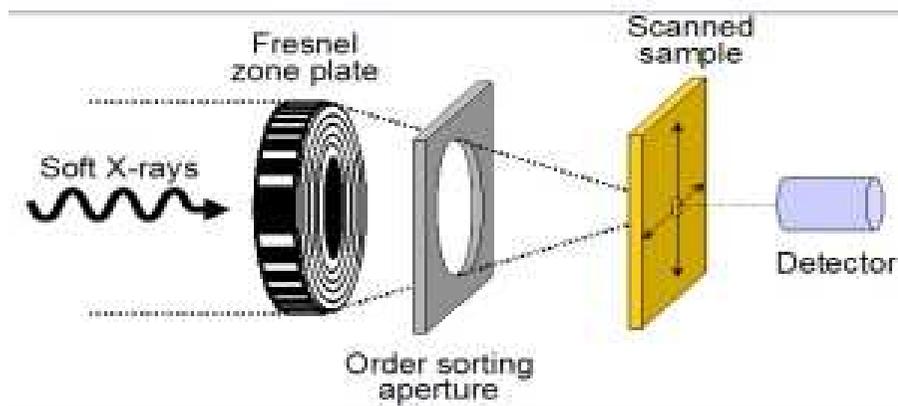
SGM beamline, CLS



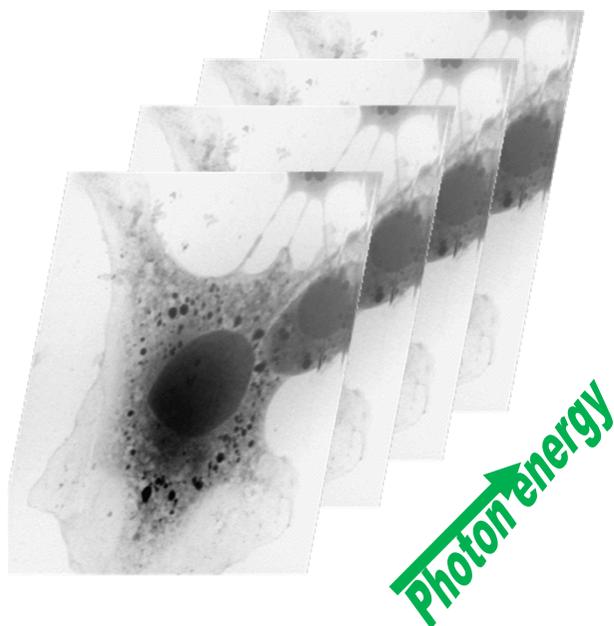
- Characterize C and N functional groups of soil organic matter without any pretreatment.
- Spot Size: 1000*100 MICRONS

Advanced Characterization Techniques

Scanning Transmission X-ray Microscopy (STXM) –NEXAFS



SM beamline, CLS



Acquire sequence of images over NEXAFS spectral region at 30-40nm resolution

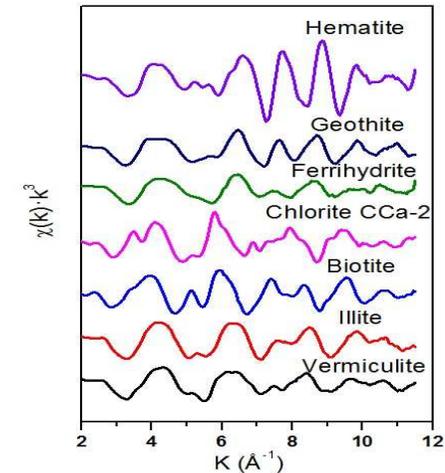
- Map distribution of C and C forms and the major elements (K, Ca, Fe, Al, Si) in soils at nanometer scale.
- Assess the interactive mechanisms of C with specific soil minerals.

Advanced Characterization Techniques

Iron Speciation

Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS):

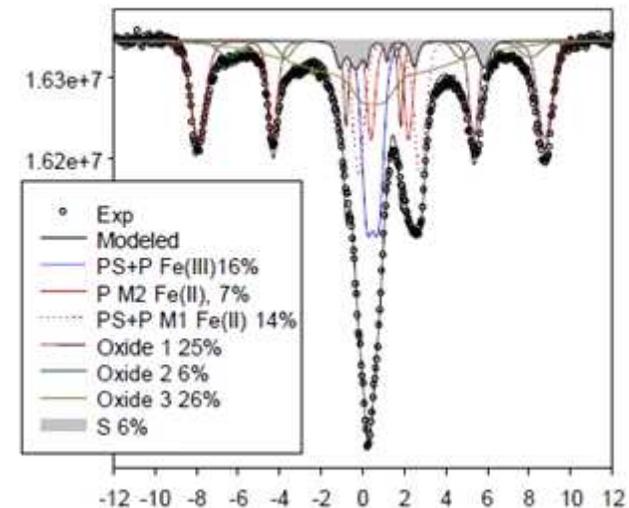
Linear Combination Fitting of standard spectra to unknown spectra



Mössbauer Spectroscopy:

A suitable tool to tease apart Fe oxides from each other and from Fe-phyllosilicates in soils and sediments.

d) 51.5-51.8 m (12 K spectrum)

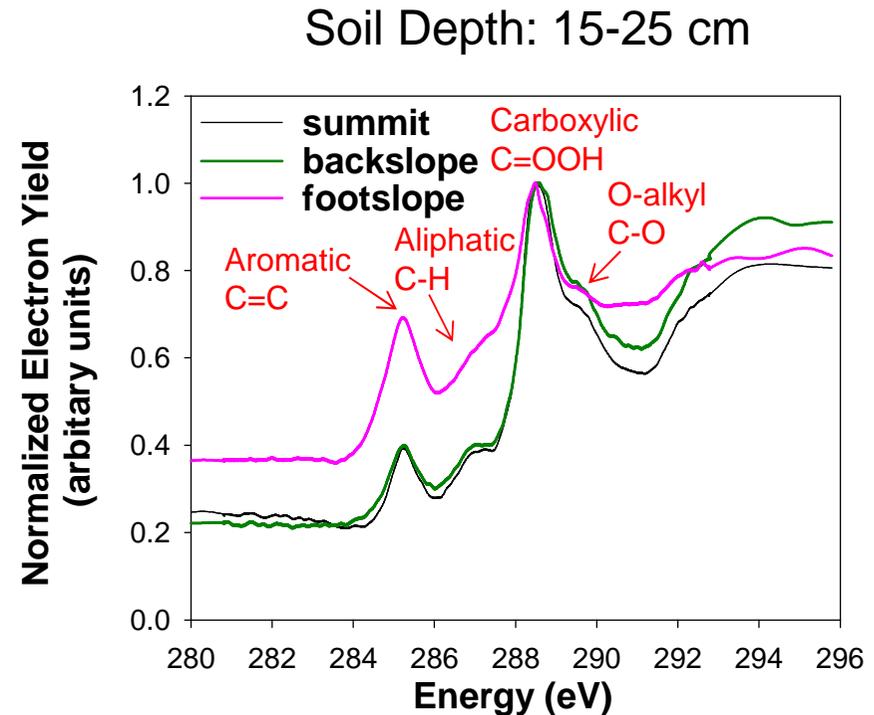
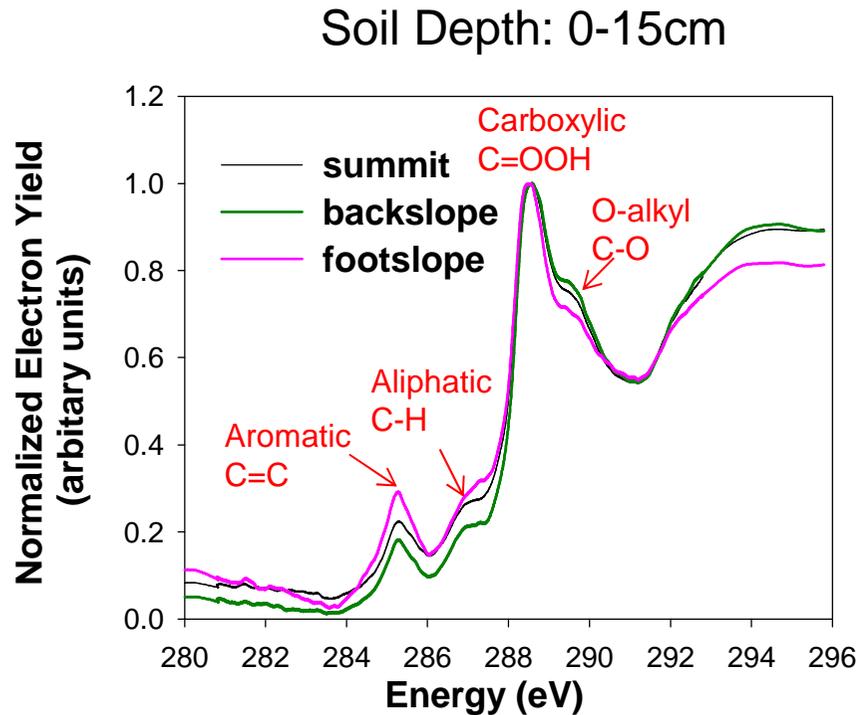


X-ray Diffraction (XRD):

Identify clay mineralogy

STXM-NEXAFS Analysis of Pasture Soil

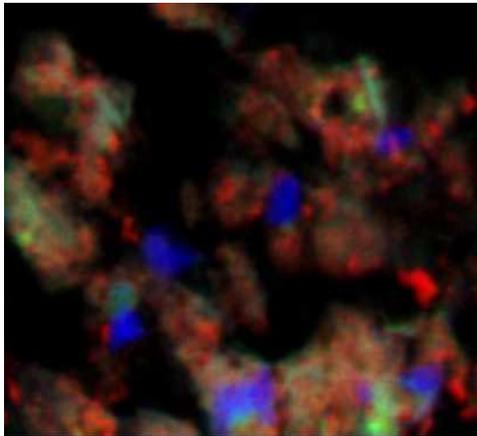
Pasture Soil Carbon Speciation by NEXAFS



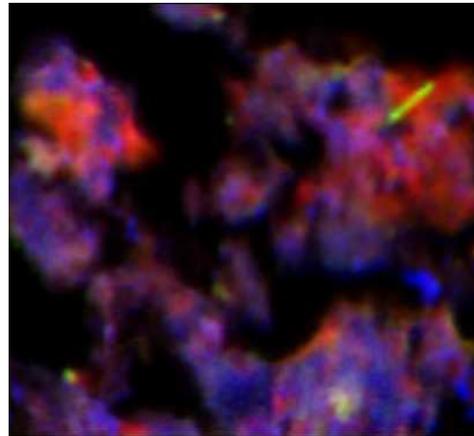
Footslope soil: enriched in aromatic C=C
depleted in aliphatic C-H

Color-coded Composite Maps of C, Ca, Fe, Al and Si from Pasture Soil Clay Fractions

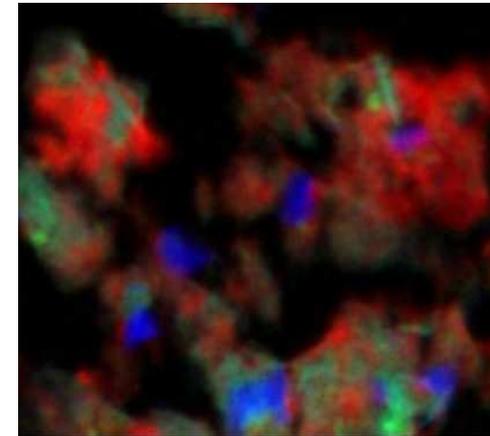
Fe Al Si



C Ca Fe



C Al Si



Fe is intimately associated with Al and Si .

Discrete quartz particles.

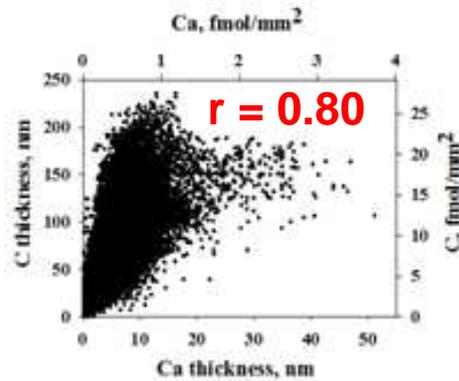
C is closely associated with clay particles, as particulate organic matter has been excluded from the clay fractions.

The discrete SiO₂ particles contain little or no C

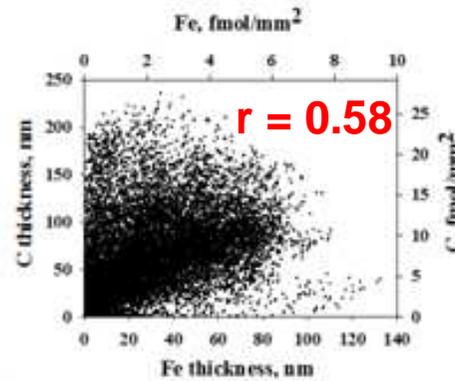
Correlation between C and Ca, Fe, Al, & Si

Summit Soil

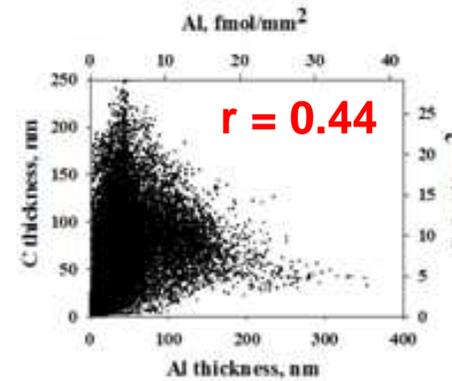
Ca



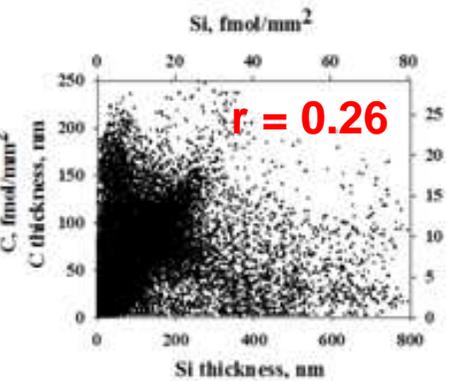
Fe



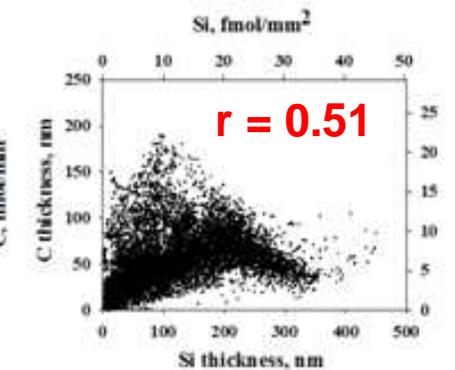
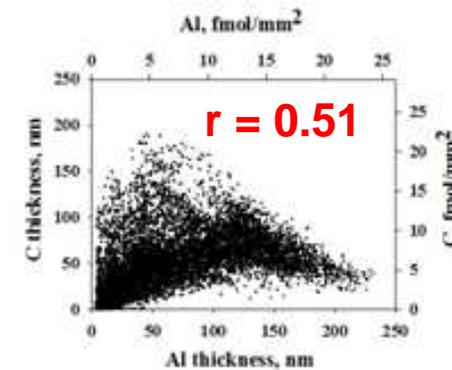
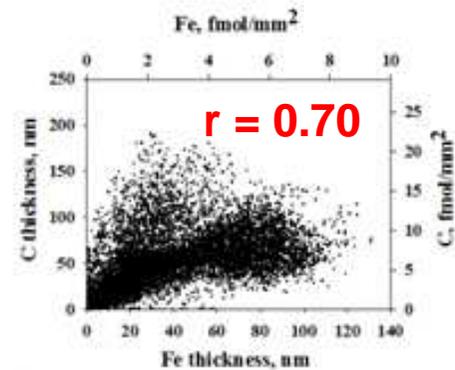
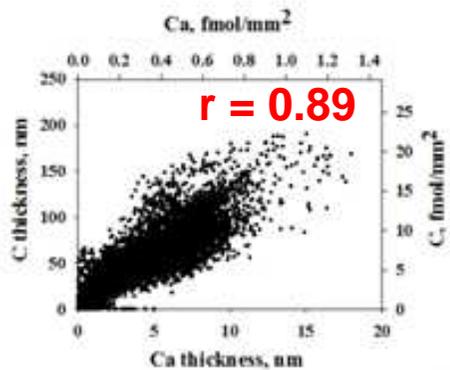
Al



Si



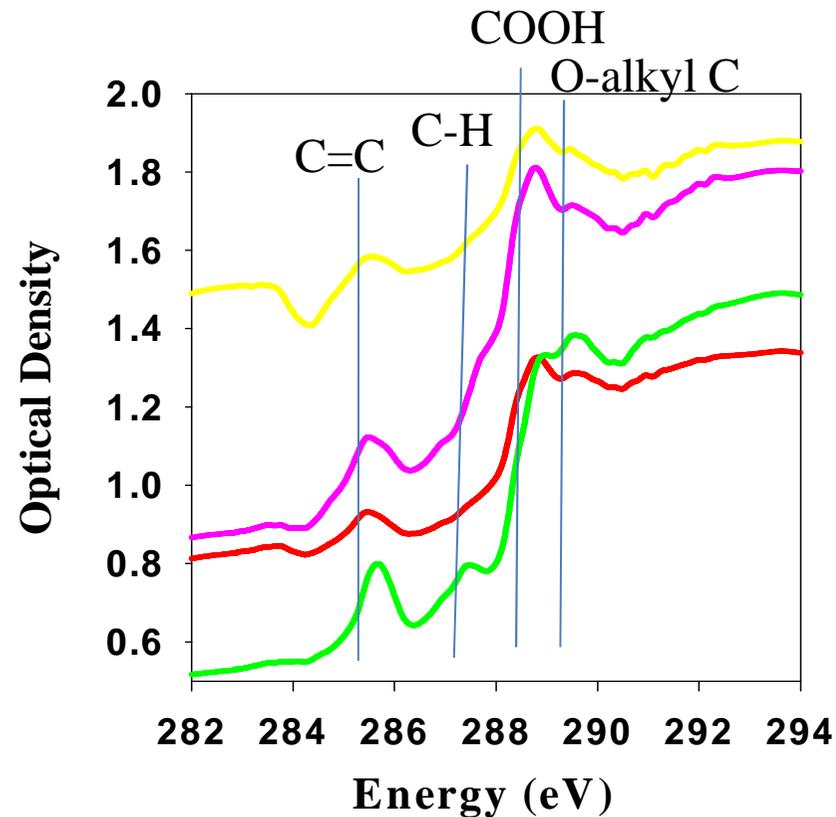
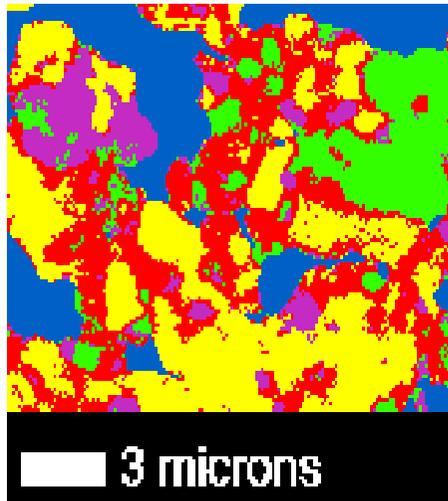
Footslope Soil



Good C-Ca Correlation

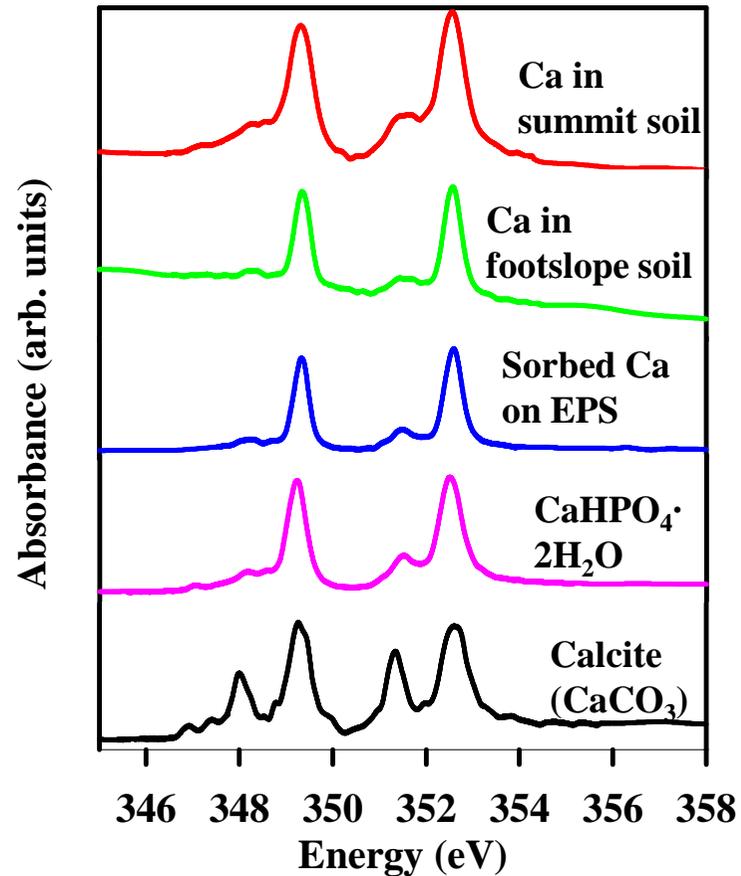
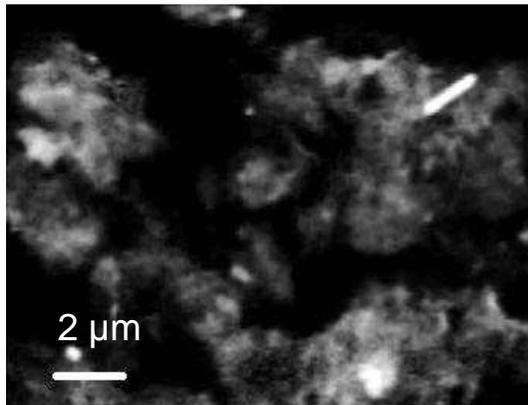
Better correlation of C with Fe than Al & Si

Distribution of C Functional Groups



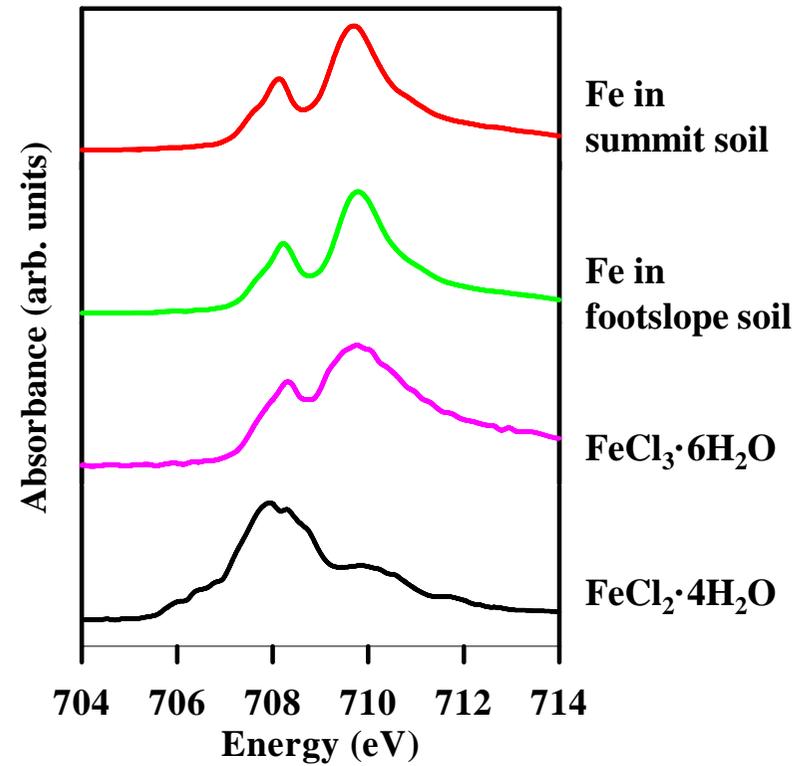
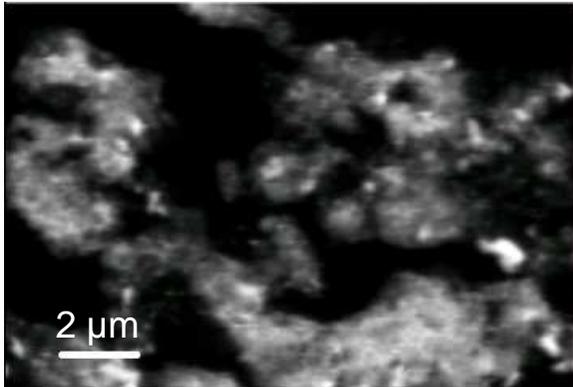
The majority of OM forms associated with soil organo-mineral assemblage are aromatic C=C, carboxylic-C and polysaccharides

Ca Distribution and Speciation



Ca forms: organically complexed Ca and/or Ca phosphate

Fe Distribution and Speciation



Fe³⁺ present in soils. No Fe²⁺

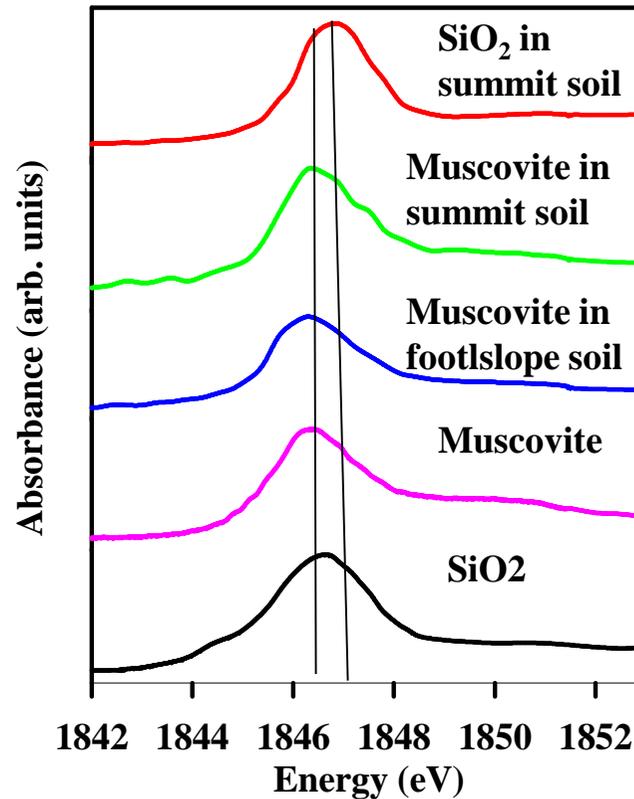
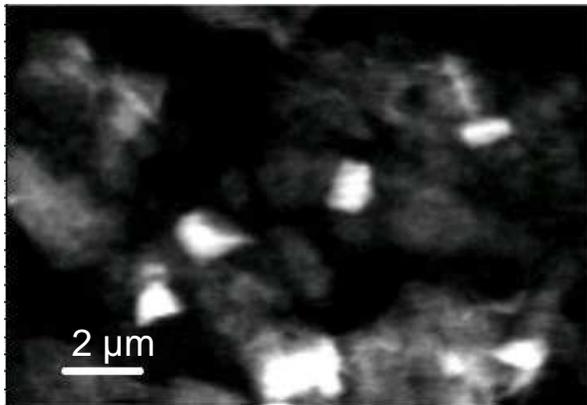
Fe EXAFS

	Fe(III)-aluminosilicates		Fe(III) oxides		
	Vermiculite (%)	Illite (%)	2-line ferrihydrite (%)	Goethite (%)	Hematite (%)
Summit	35	15	9	18	23
Footslope	32	12	16	24	16

About 50% of total Fe is in Fe(III) oxides.

Fe(III) oxides are mainly crystalline goethite and hematite.

Si Distribution and Speciation



Quartz particles present in clay fractions

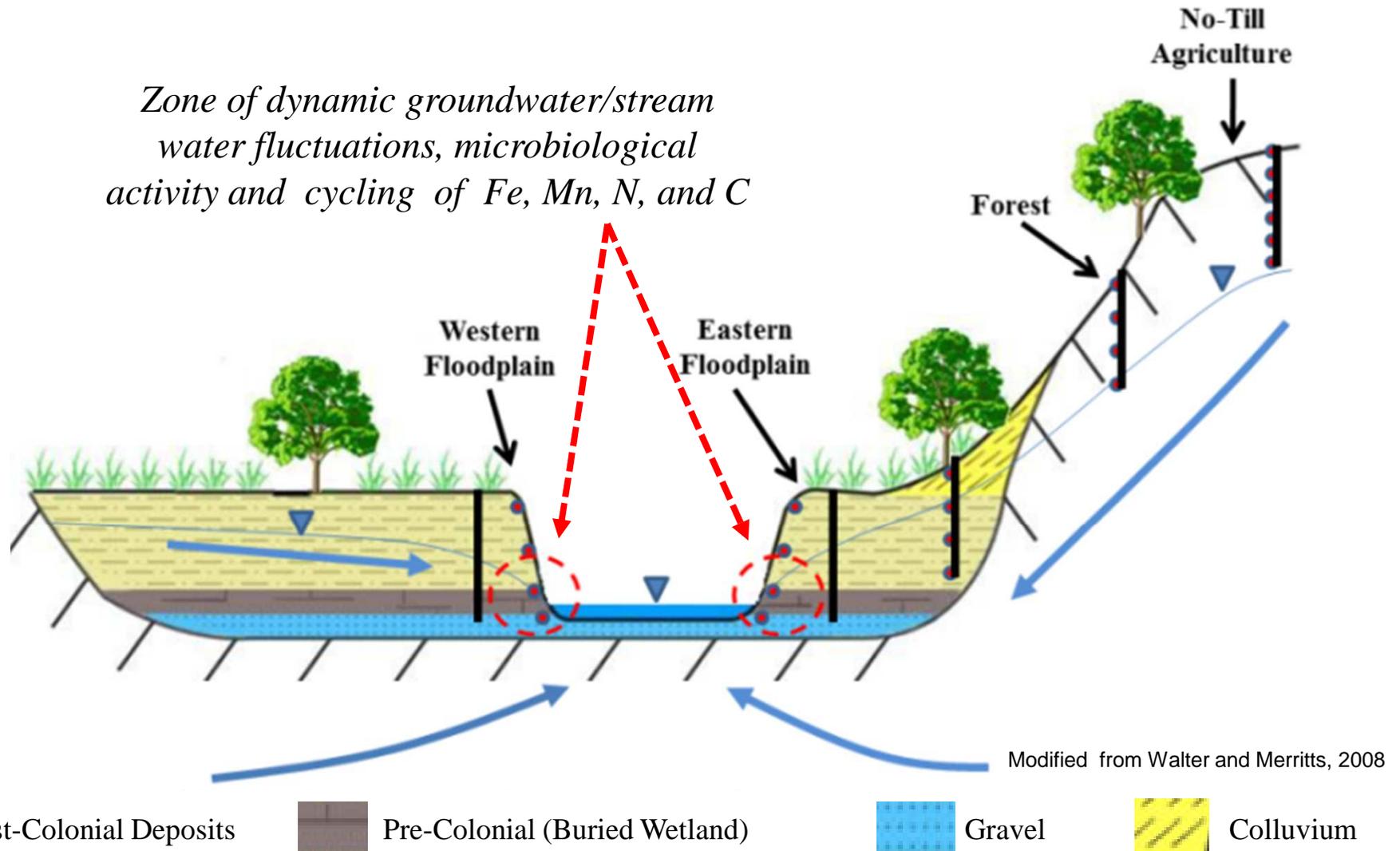
Clay aluminosilicates in the soils are hydroxy-interlayered vermiculite, illite and kaolinite by XRD

Solid-phase Iron Speciation Under Varying Redox Environments

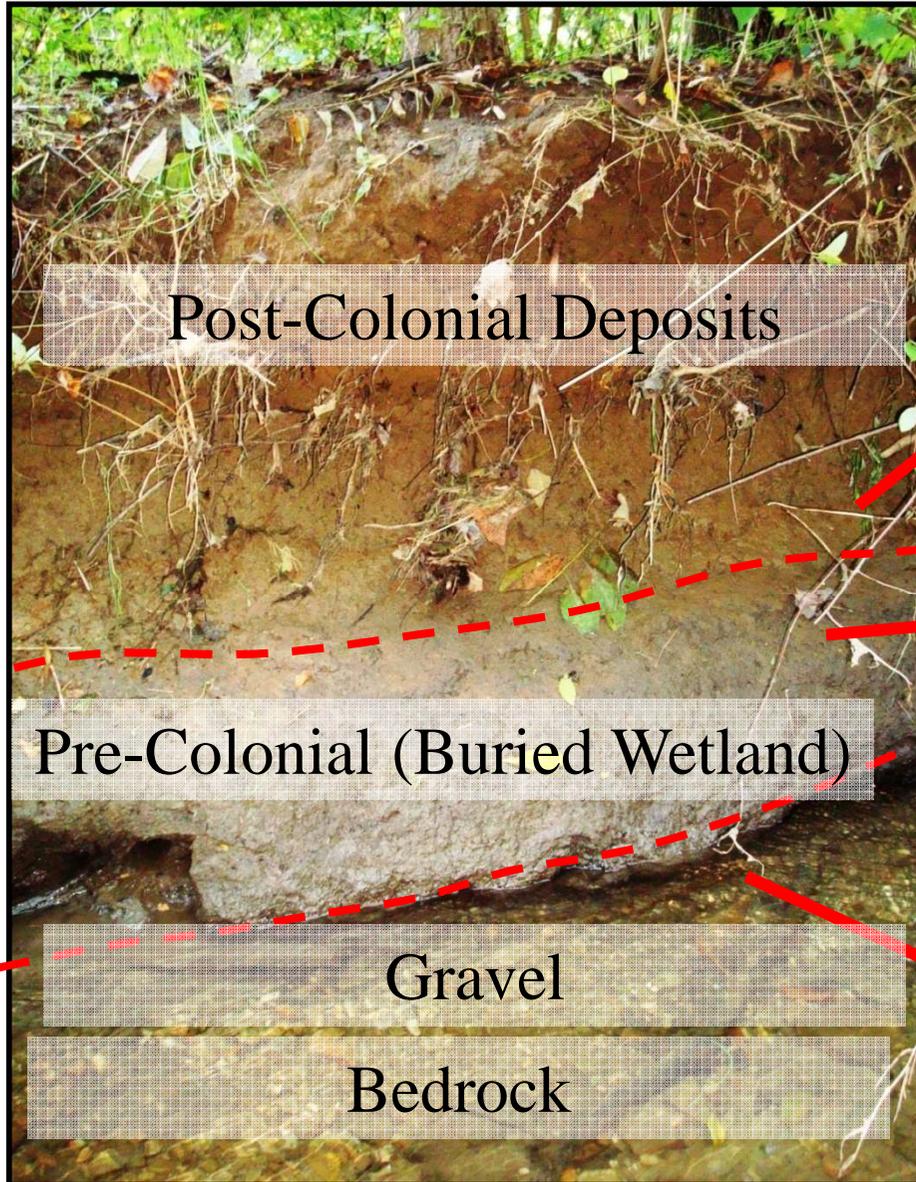
Research Conceptual Model

Role of Fe- and Mn- redox transformations on carbon cycle and sequestration in a mixed land use watershed, including floodplain forest, upland forest and agriculture

Zone of dynamic groundwater/stream water fluctuations, microbiological activity and cycling of Fe, Mn, N, and C

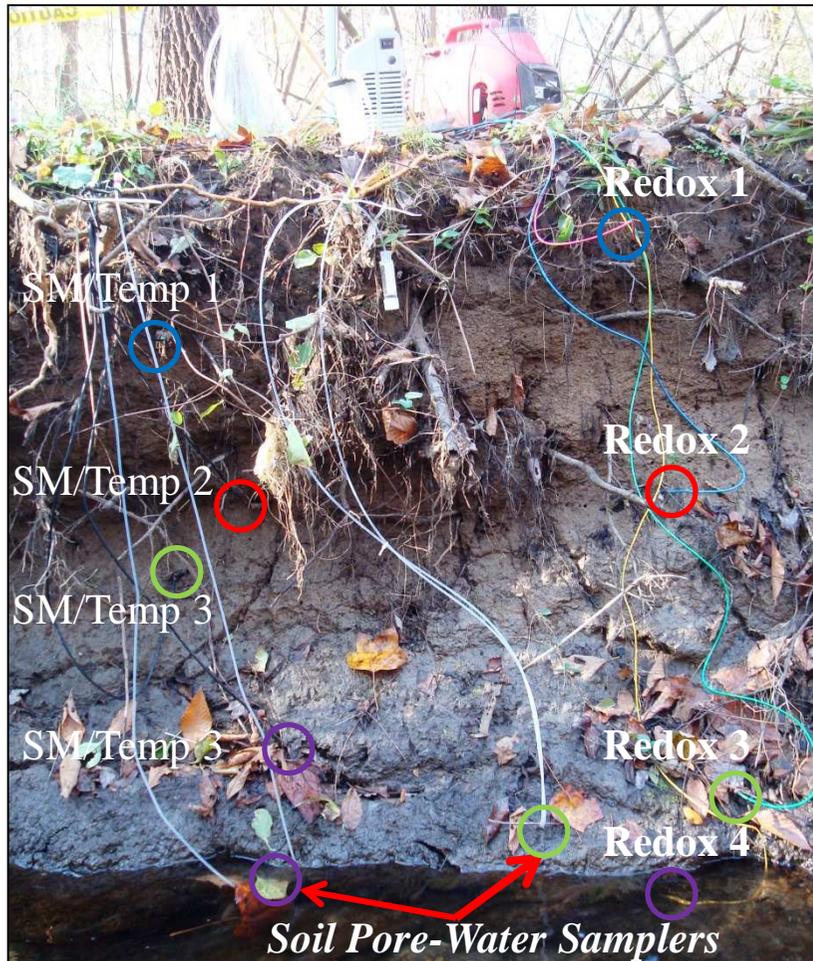


Field Sampling: Floodplain

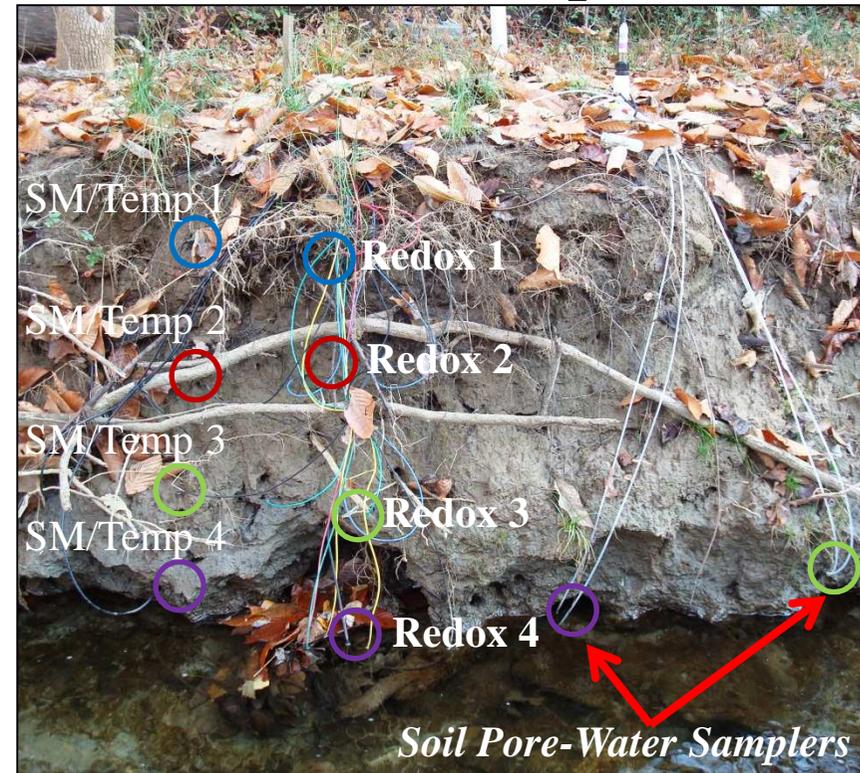


Sensor Installation and Sampling Locations

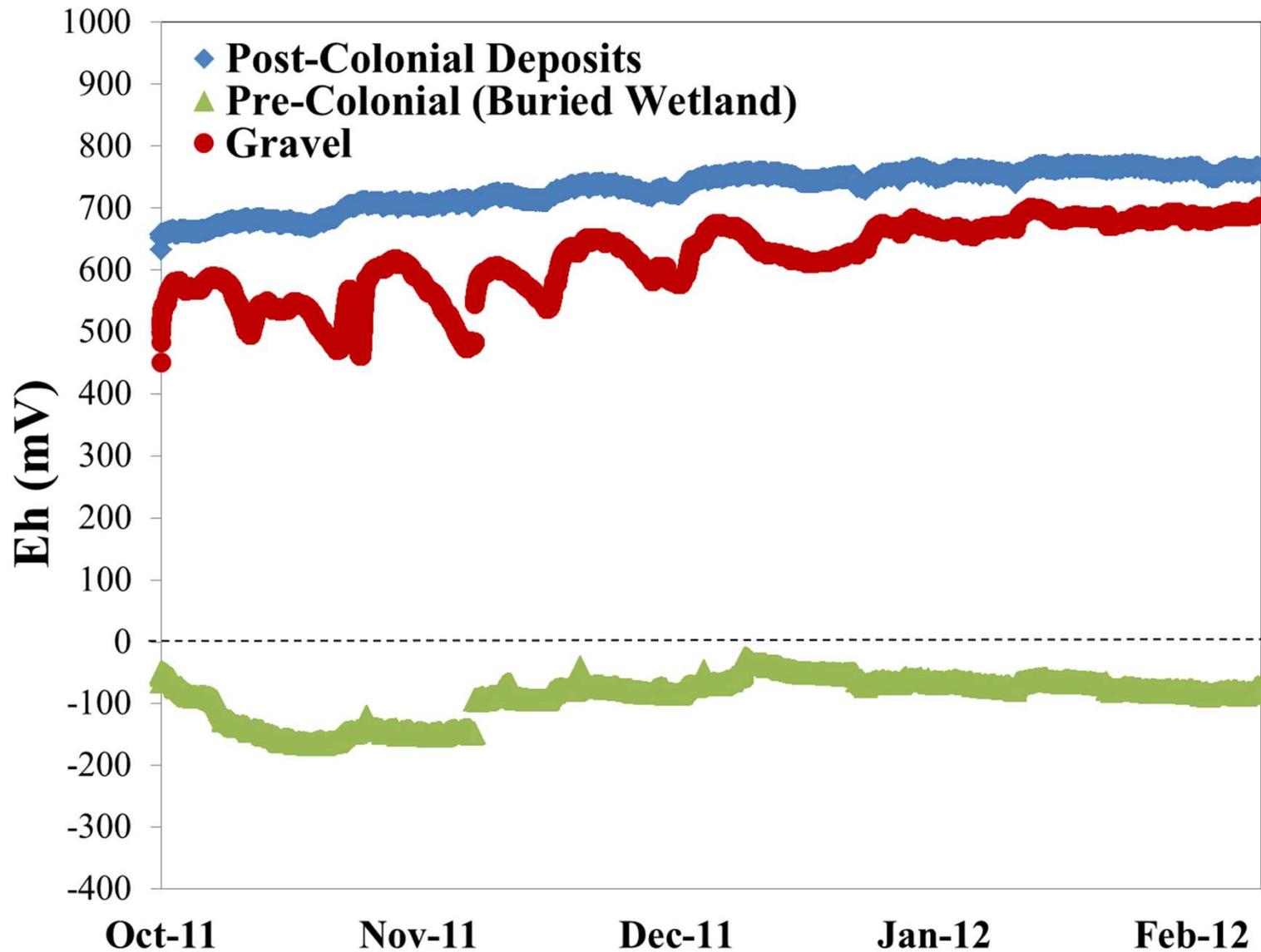
Western Floodplain



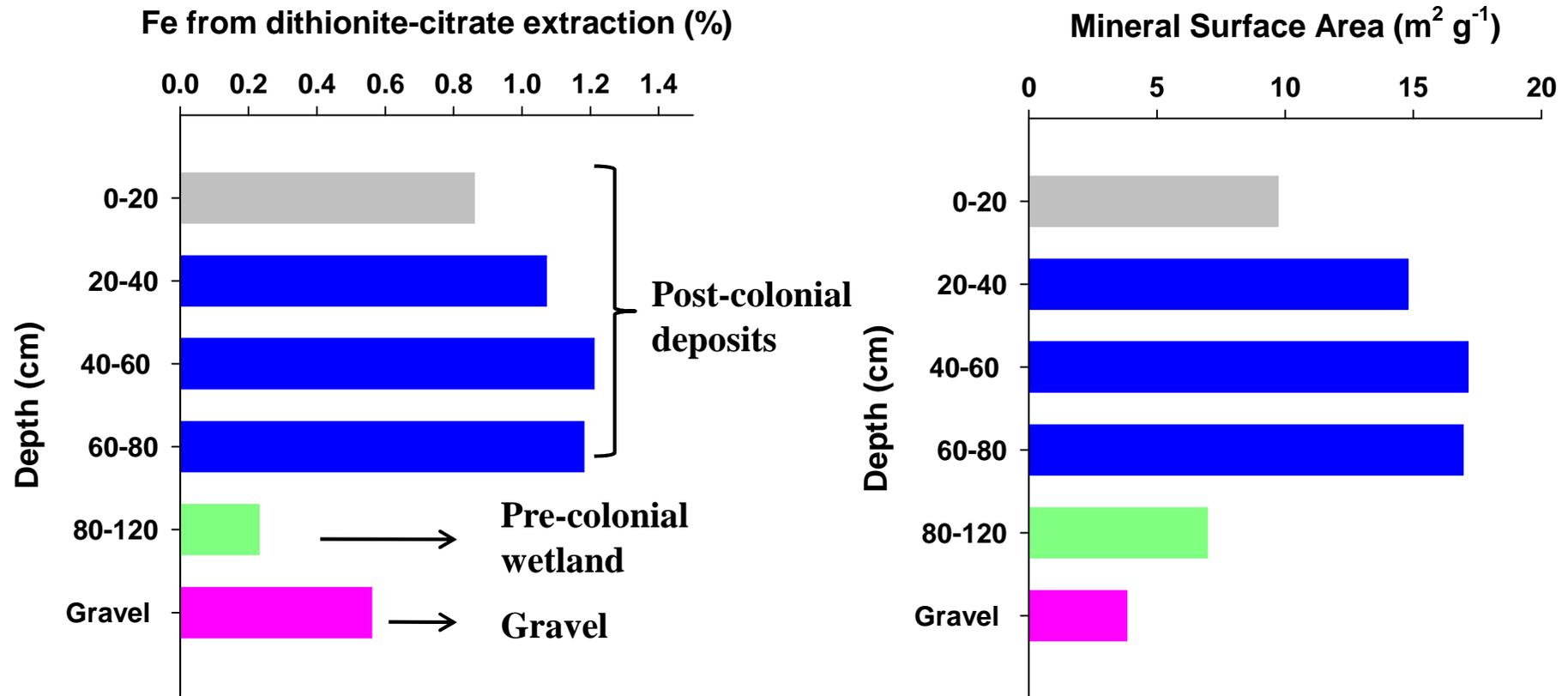
Eastern Floodplain



Continuous In-situ Monitoring of redox in Western Flooplain



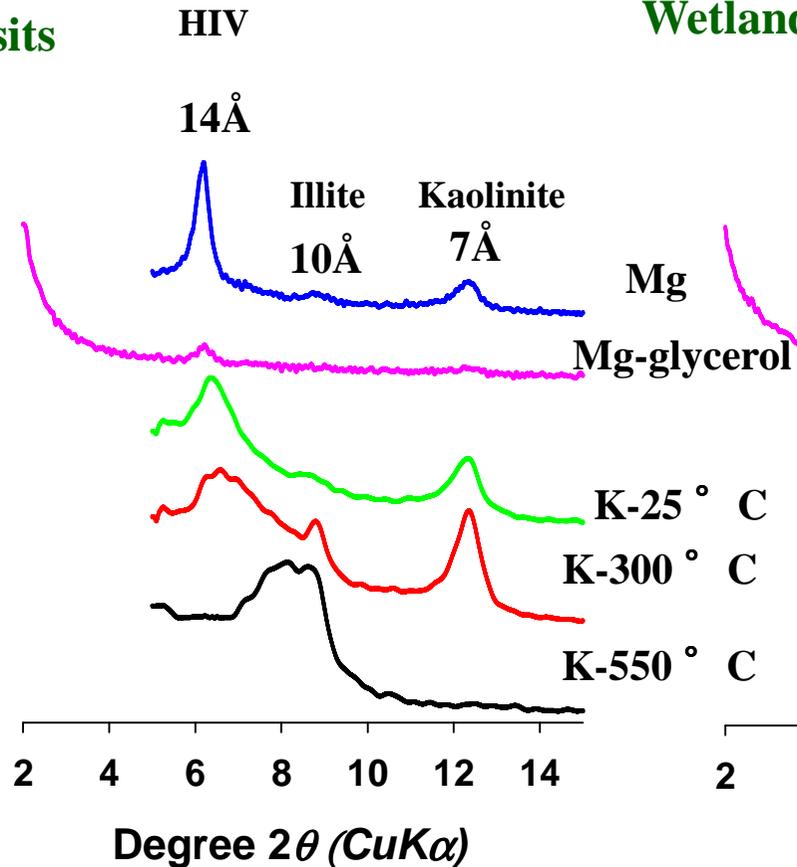
Floodplain Soil Fe Oxide Content and Mineral Surface Area



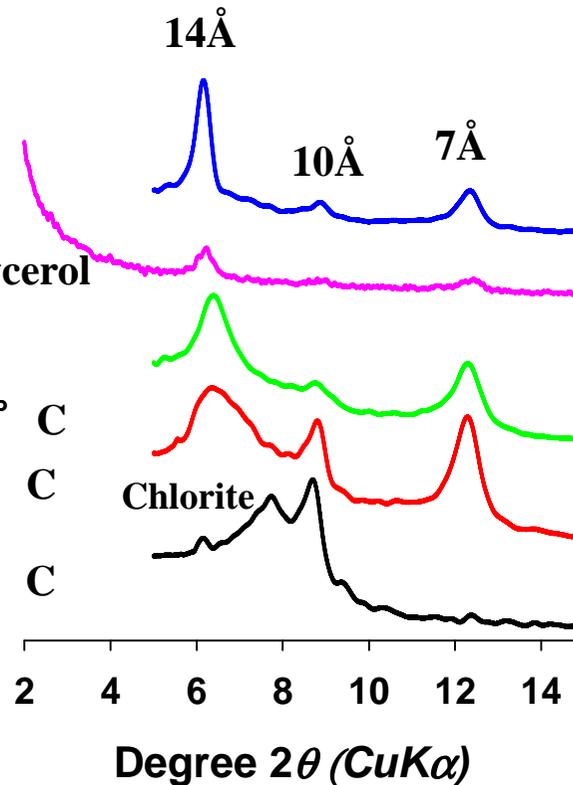
Less Fe oxides from DCB extractions and lower mineral surface area in buried wetland.

Floodplain Soil Clay Mineralogy by XRD

Post-colonial
deposits



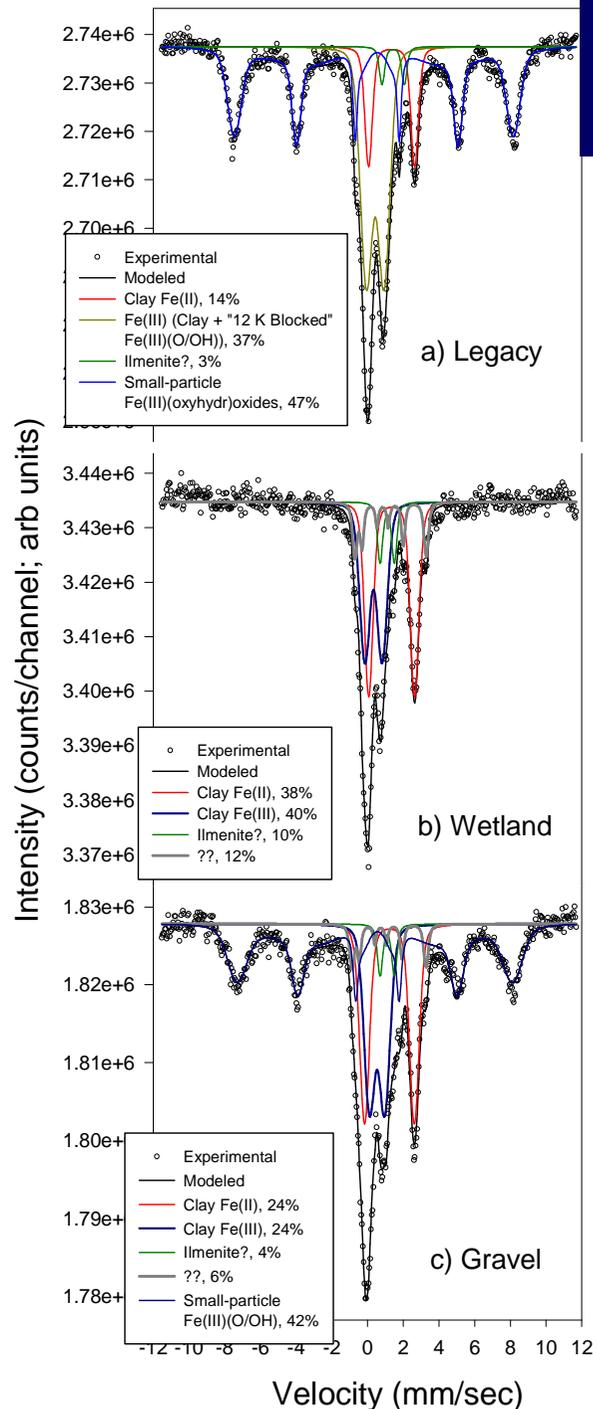
Pre-colonial
Wetland



Hydroxy interlayered vermiculite (HIV), kaolinite, and trace amounts of illite

Chlorite in pre-colonial wetland

Solid-phase Iron Speciation by Mössbauer Spectroscopy for Floodplain Soil

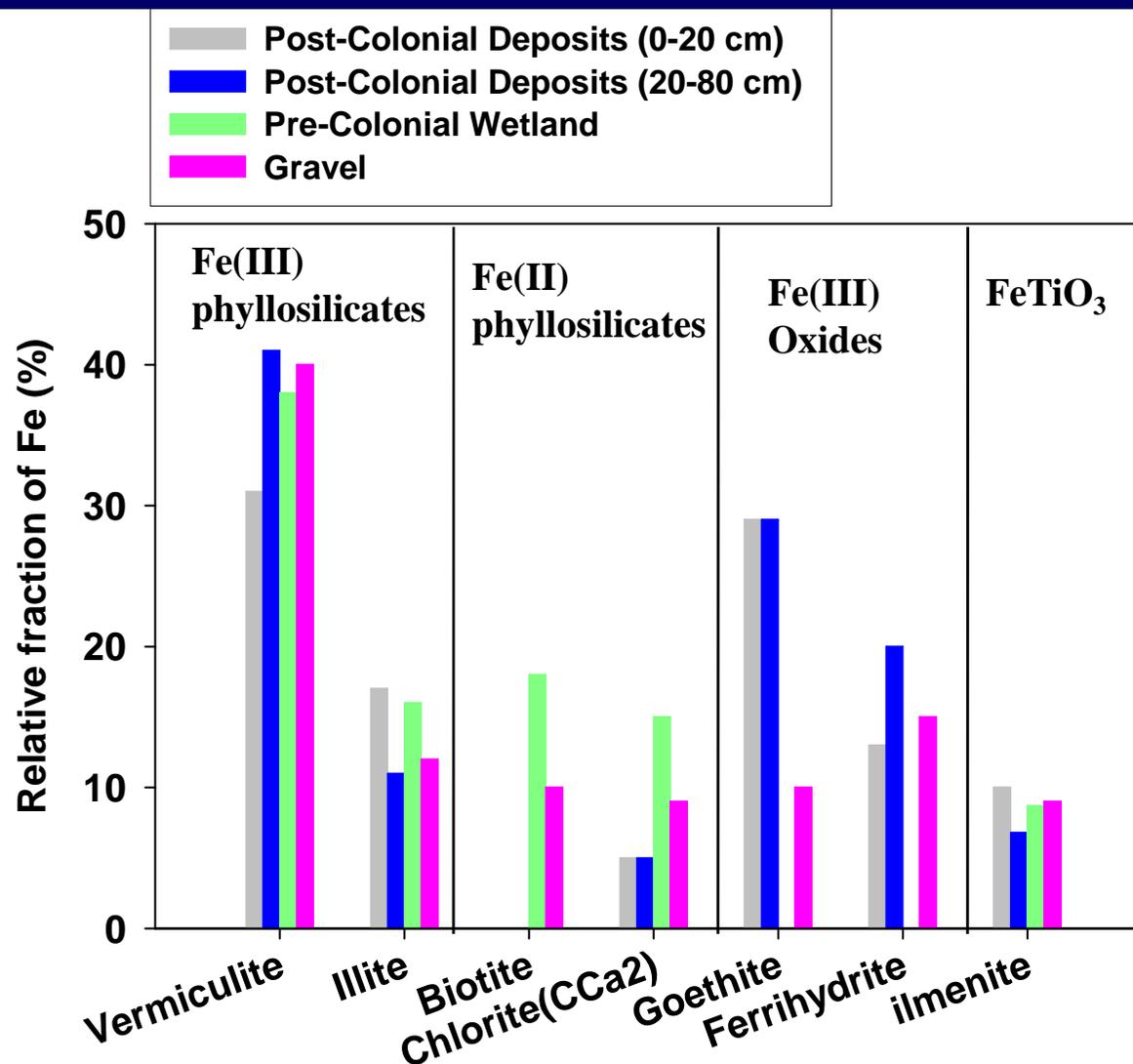
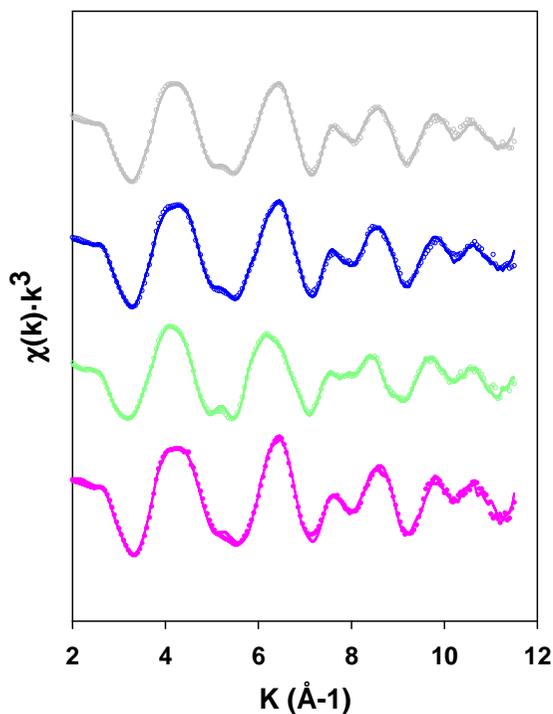


Fe(III) in clays is significantly reduced in the wetland compared to legacy sediments and gravel

Fe(III) (oxyhydr)oxides were absent in the wetland .

These findings highlight that in addition to reductive dissolution of Fe(III)-(oxyhydr)oxides, the anoxic redox conditions of the floodplain soils lead to clay structural Fe reductive cycling in the natural field.

Floodplain Soil Fe Speciation by EXAFS



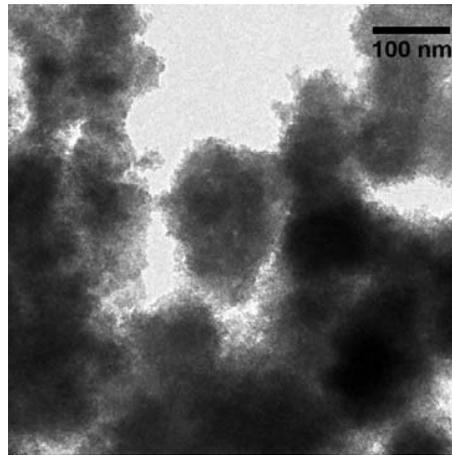
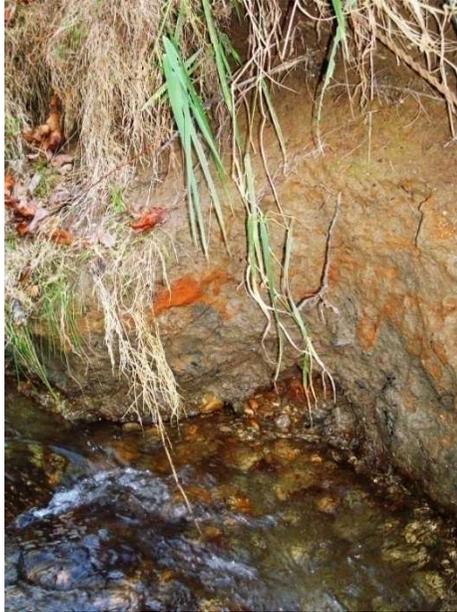
In the anoxic pre-colonial wetland:

No Ferrihydrite

Fe(II) phyllosilicates: biotite and chlorite CCa-2

**Stabilization of Organic Matter by Adsorption and
Coprecipitation with Ferrihydrite: A Laboratory
Study**

Ferrihydrite: Amorphous Fe Oxides



- Ubiquitous occurrence in the environment
- Small particle size
- High surface area: $\sim 300 \text{ m}^2/\text{g}$
- Highly reactive with organic matter in soils and sediments
- Forms in the presence of organic matter

Cismasu et al, 2012

Research Objectives

- Investigate the extent of organic matter adsorption and coprecipitation with ferrihydrite
- Compare the stability of the adsorbed and coprecipitated organic matter
- Compare the mechanisms of organic matter-ferrihydrite complex formation by adsorption and coprecipitation
- Examine the spatial distribution of organic matter on ferrihydrite at the nanometer-scale

Experimental Setup

Adsorption:

Dissolved Organic Matter (DOM): from forest litter layer

Mixing DOM solution with freshly synthesized ferrihydrite (pH 4 and 7)

Coprecipitation:

Dissolve Fe^{3+} in DOM solution and then raise pH to 7

Desorption:

0.1 M NaH_2PO_4 , 0.1 M NaOH , and 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$

Advanced Characterization:

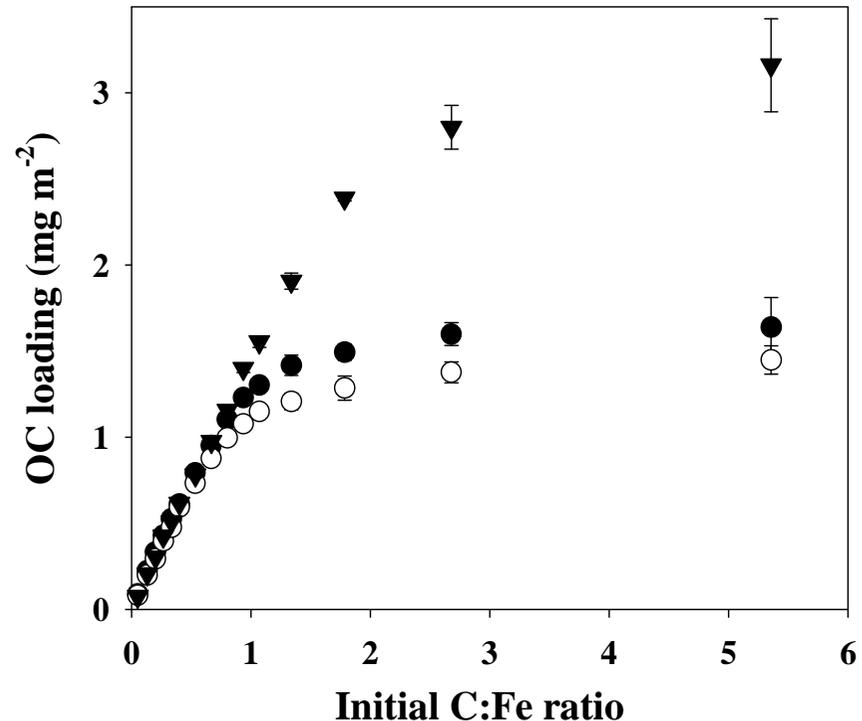
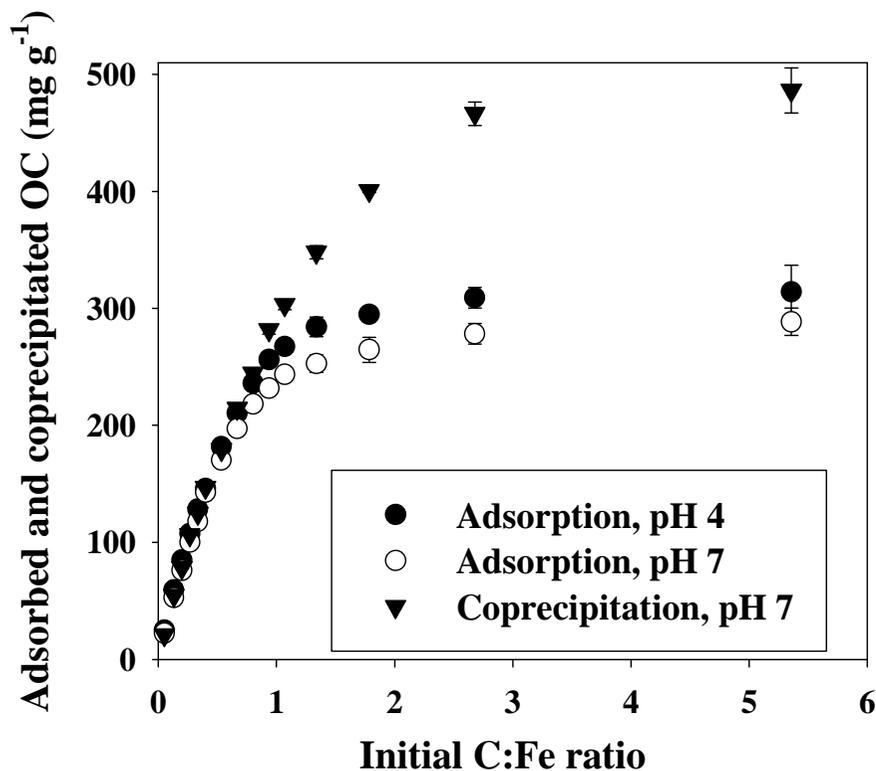
FTIR

Near-edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

Scanning Transmission X-ray Microscopy (STXM)

Fe K-edge Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy

Adsorption and Coprecipitation of DOM as a Function of the Initial C/Fe Ratios

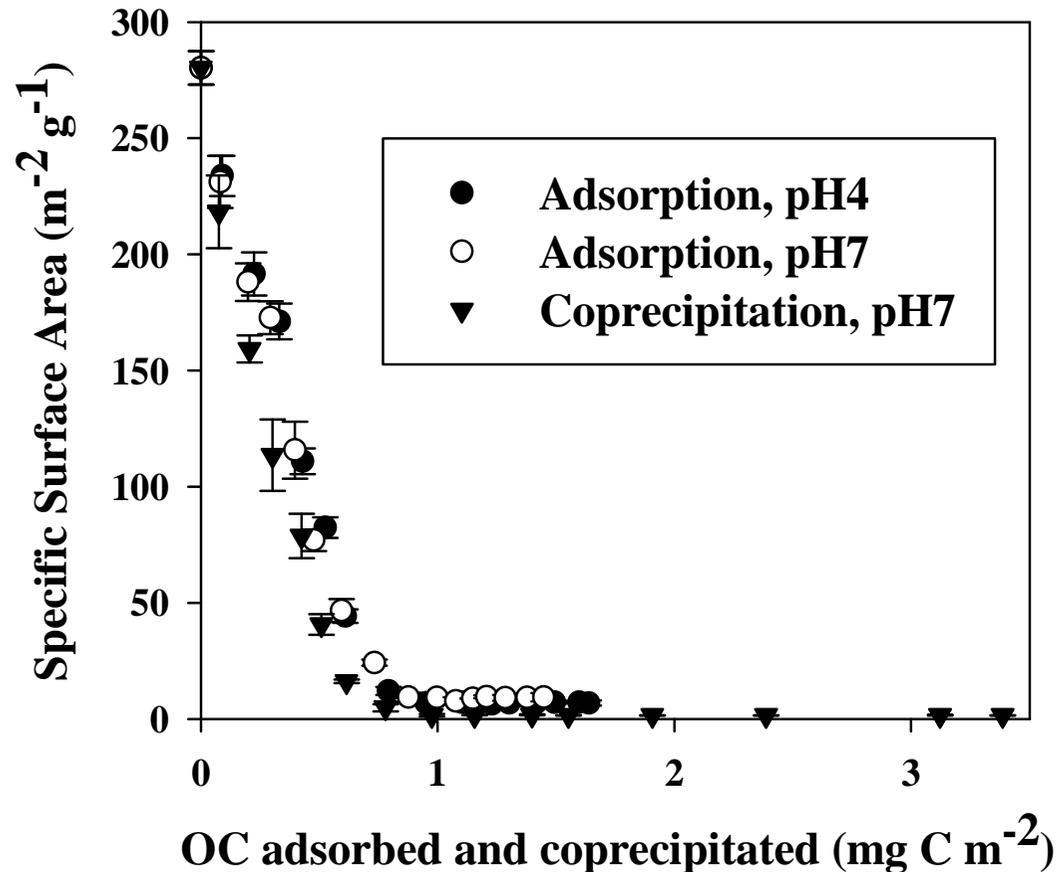


OC loadings refer to the normalized C content to the initial surface area of ferrihydrite.

Sorbed C decreases with increasing pH.

Coprecipitation leads to a greater maximum OC retention capacity than adsorption.

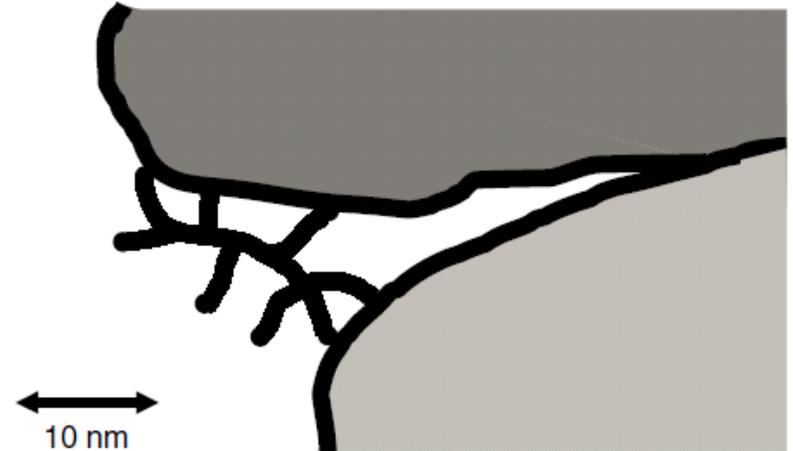
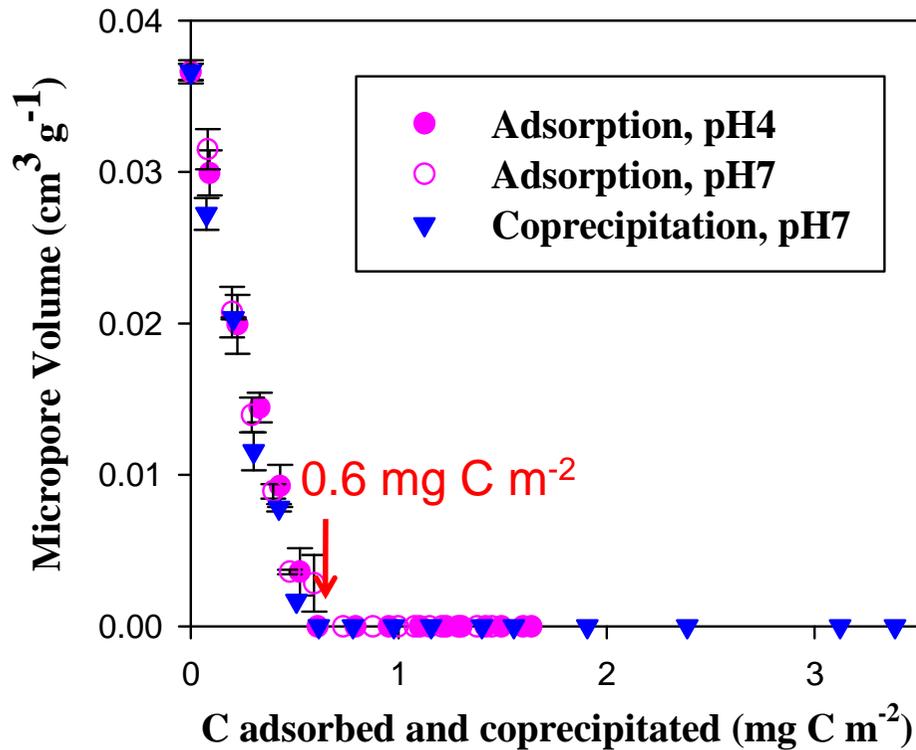
Changes in Specific Surface Area (SSA) for OM-Ferrihydrite Complexes



Ferrihydrite achieved full C coverage at C loadings of 0.88-0.97 mg C m^{-2} SA.

Multilayer C on ferrihydrite is likely to be formed at C loadings $> 1 \text{ mg C m}^{-2}$ SA.

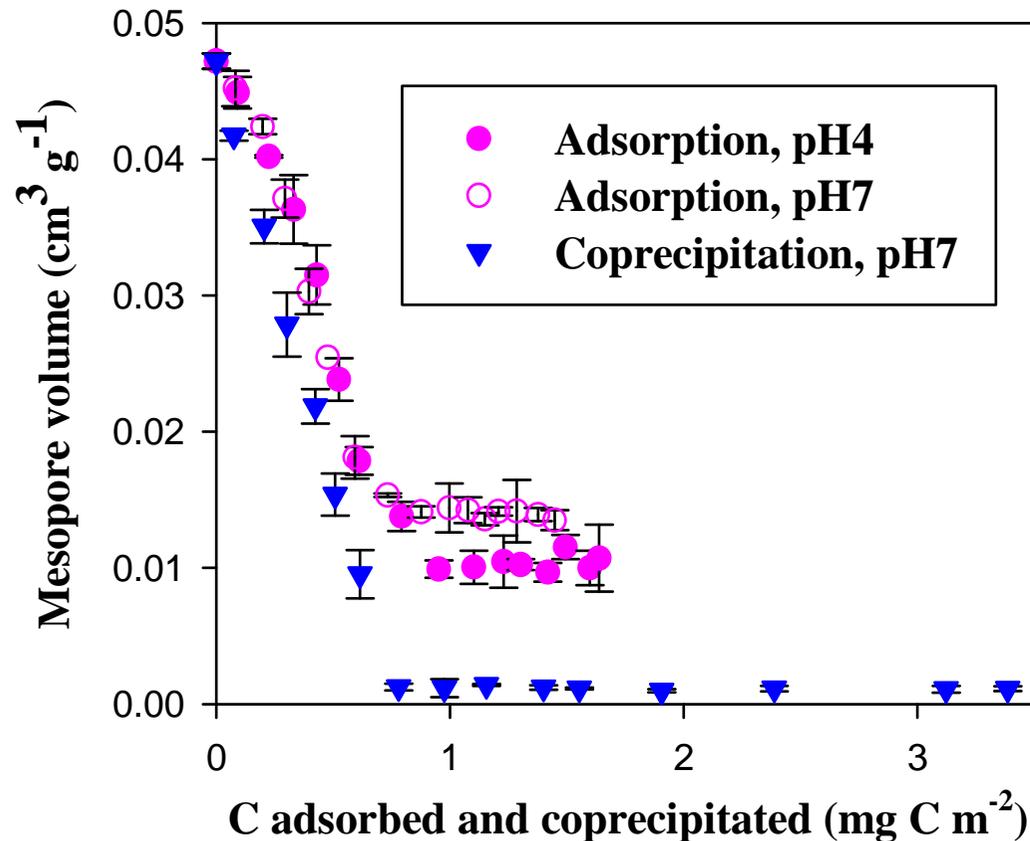
Micropore (< 2 nm) Volume



Kaiser and Guggenberger, 2003

Sorption of OM at the openings of micropores clogged and rendered them inaccessible

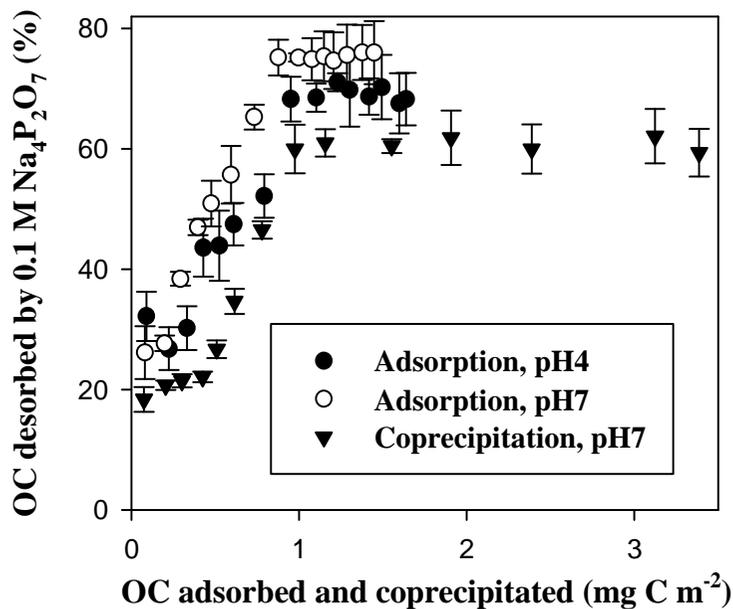
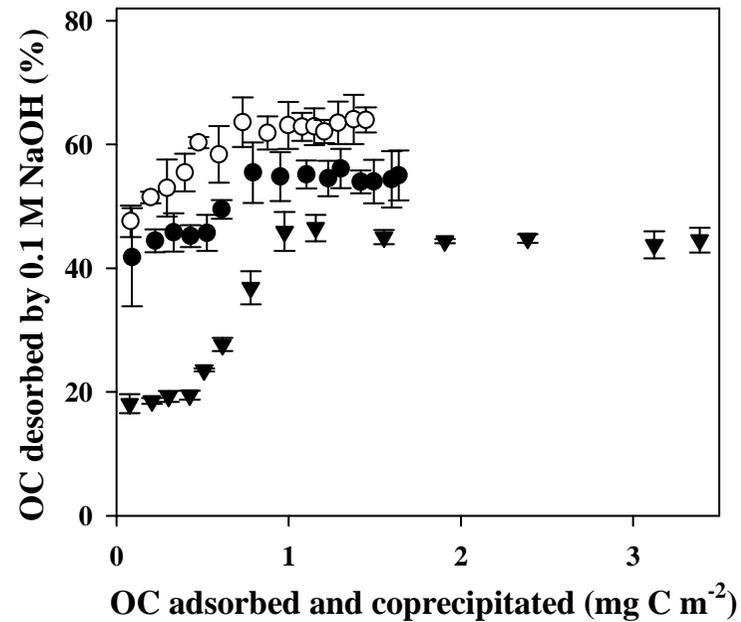
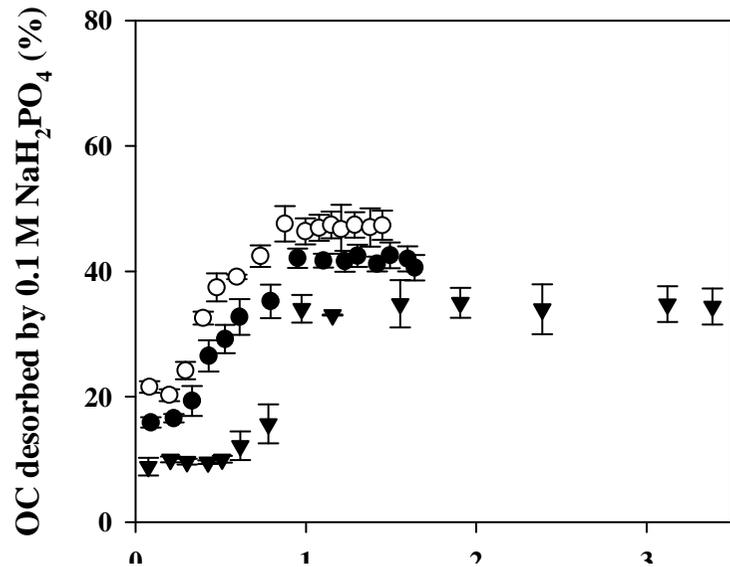
Mesopore (2-50 nm) Volume



Organic matter can enter into mesopores, thus becoming stabilized.

Coprecipitation results in greater decrease in mesopore volume than adsorption, suggesting more C is stabilized in mesopores during coprecipitation.

Desorption of Adsorbed and Coprecipitated C on Ferrihydrite

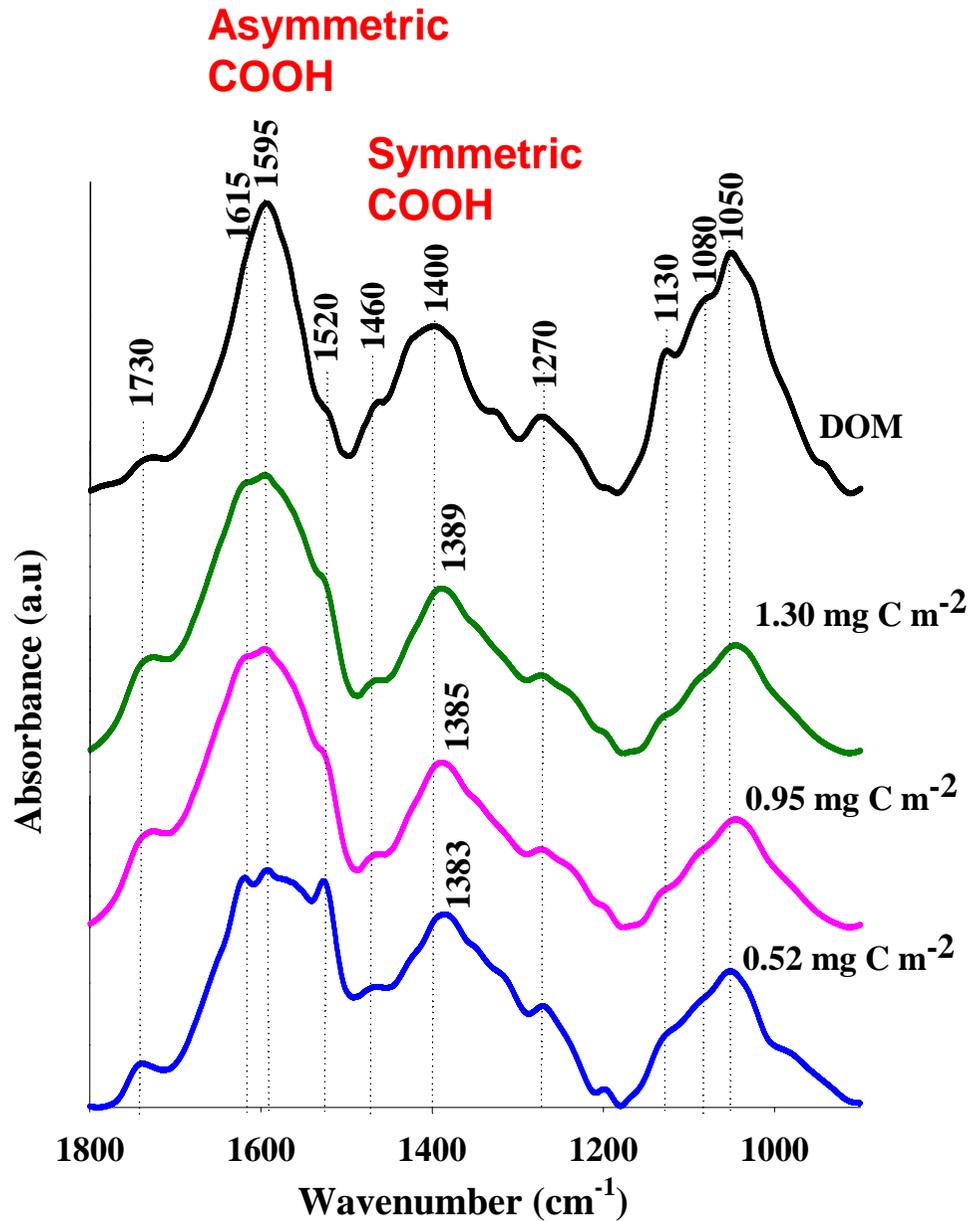


Desorption efficiency: $0.1\text{M Na}_4\text{P}_2\text{O}_7 > 0.1\text{M NaOH} > 0.1\text{M NaH}_2\text{PO}_4$

C is more stabilized at lower loadings

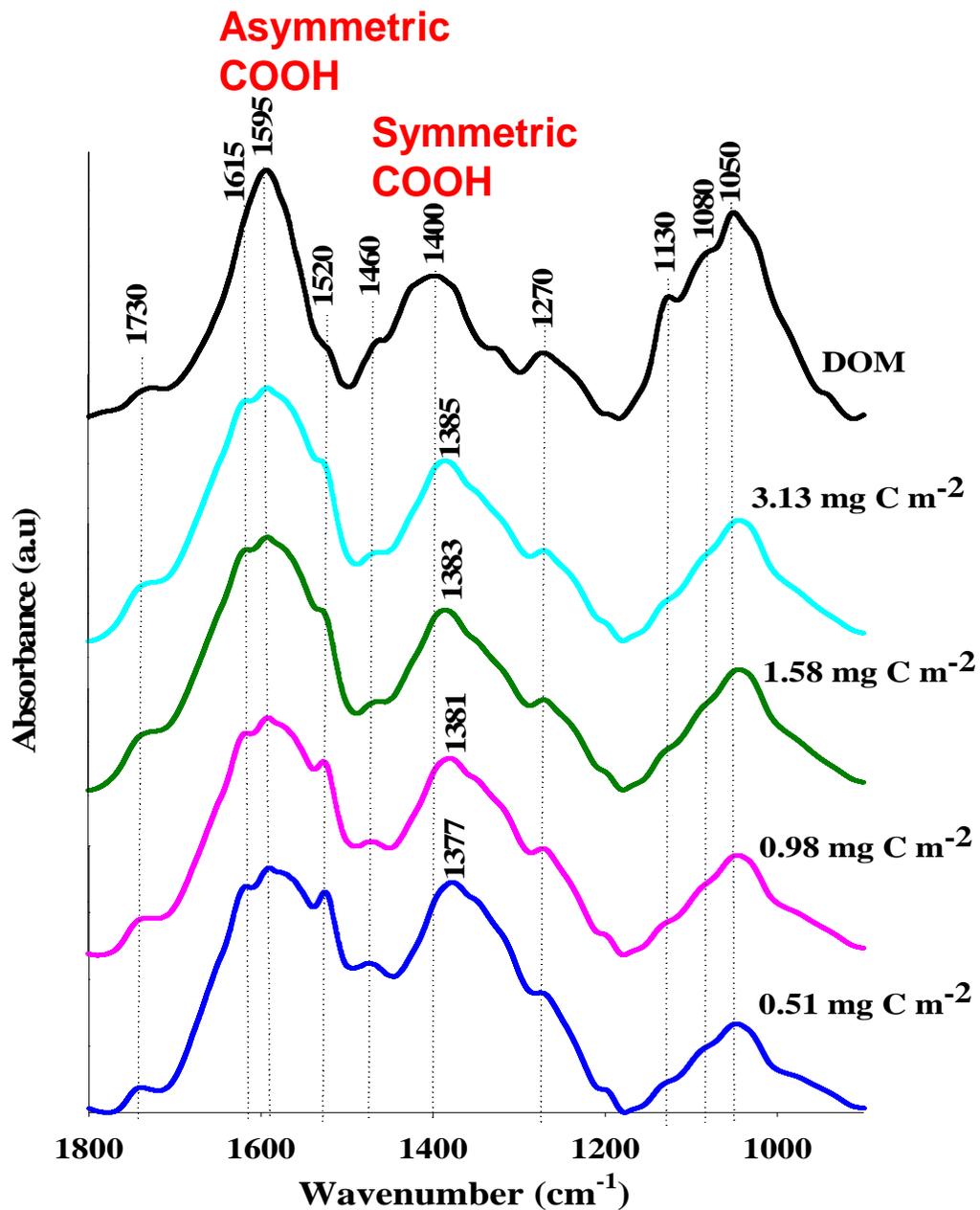
Coprecipitation leads to stronger C stabilization than adsorption

FTIR Spectra of the Adsorbed C



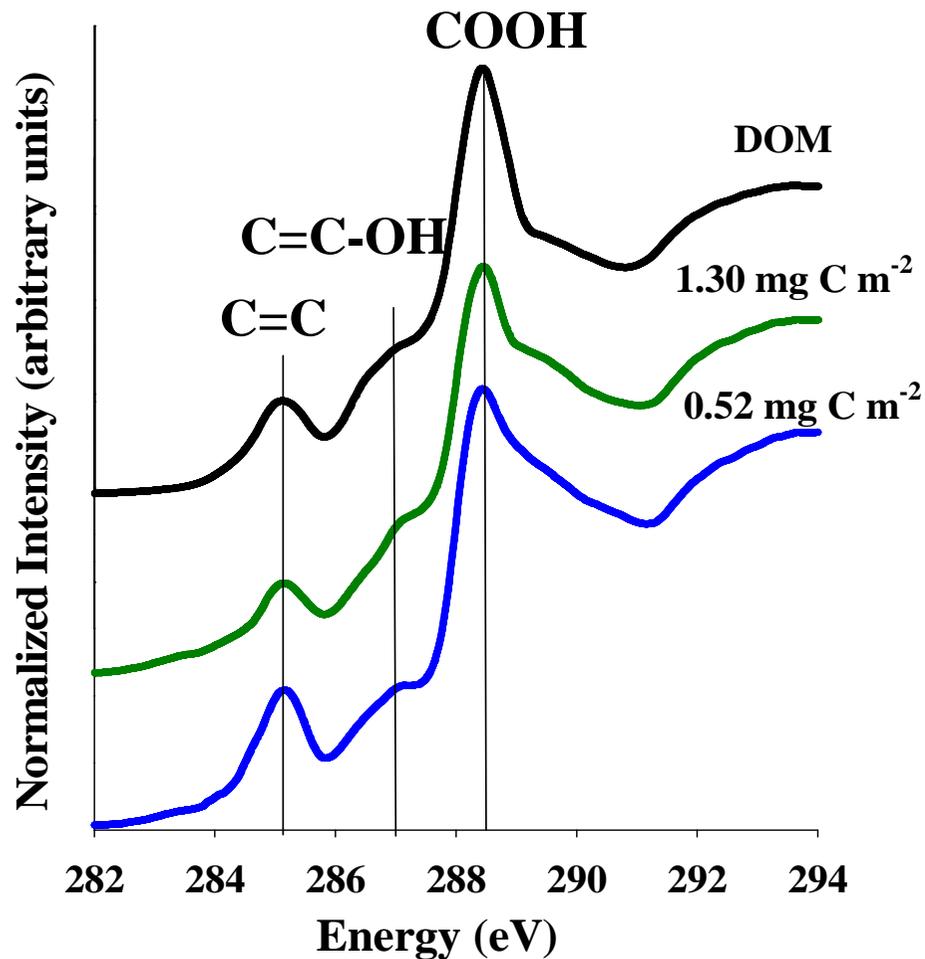
Strong complexes of carboxylic groups with ferrihydrite are formed perhaps via a ligand exchange mechanism

FTIR Spectra of the Coprecipitated C



As with adsorption, strong complexes of carboxylic C groups are formed perhaps via a ligand exchange mechanism.

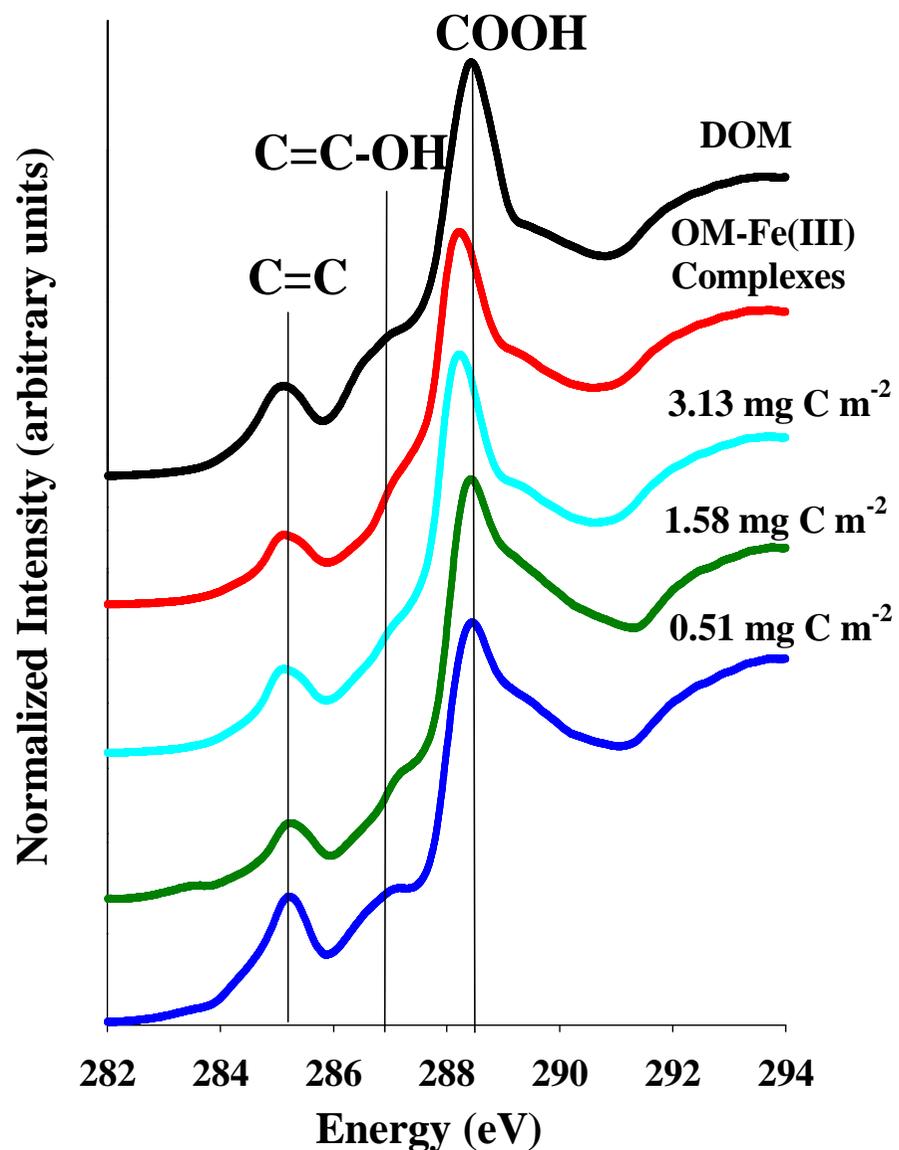
NEXAFS Spectra of the Adsorbed C



Ligand exchange between carboxylic C and ferrihydrite could be a major mechanism for OM-ferrihydrite interactions.

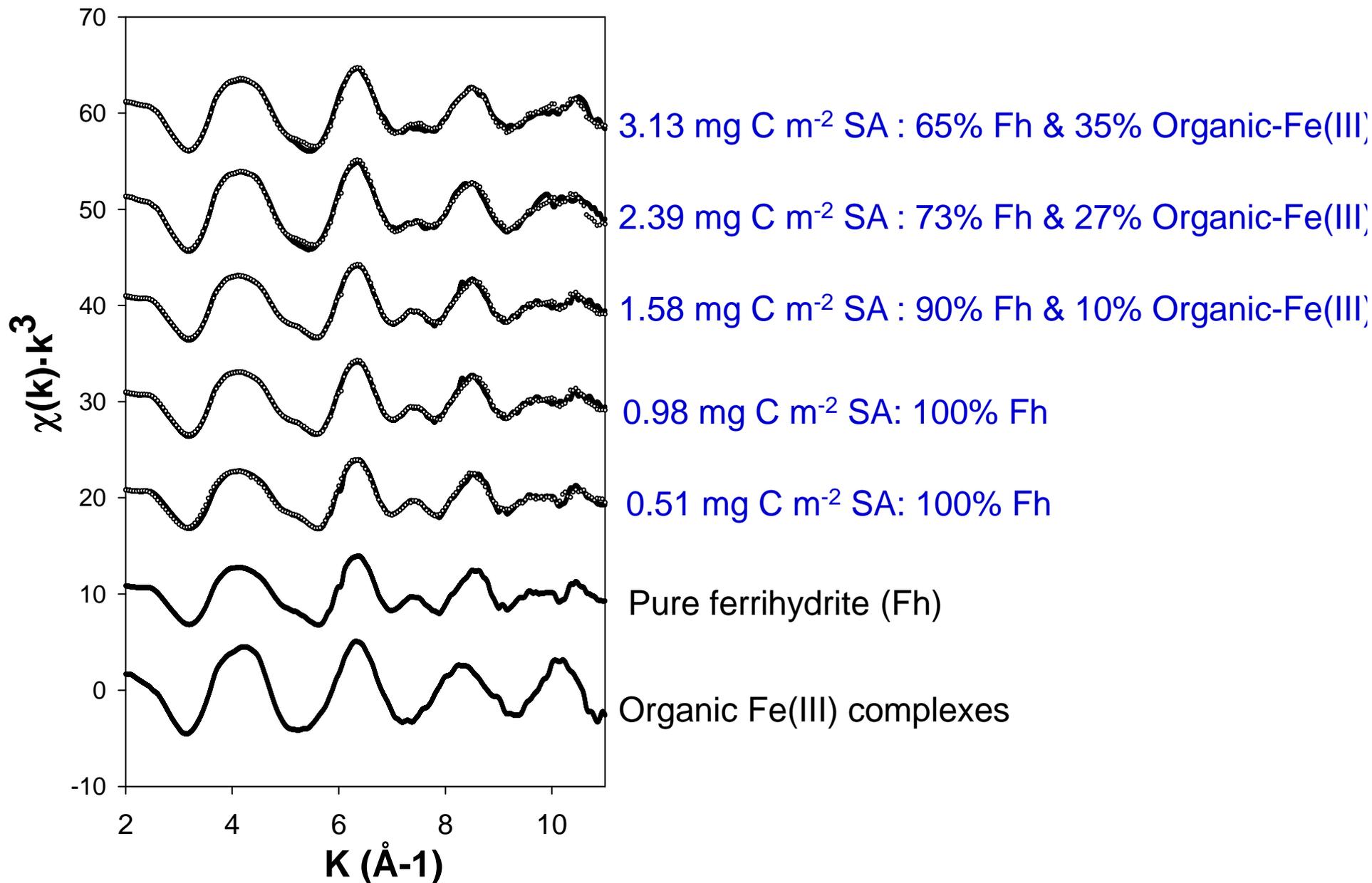
Aromatic C is selectively taken up by adsorption at lower C loadings.

NEXAFS Spectra of the Coprecipitated C



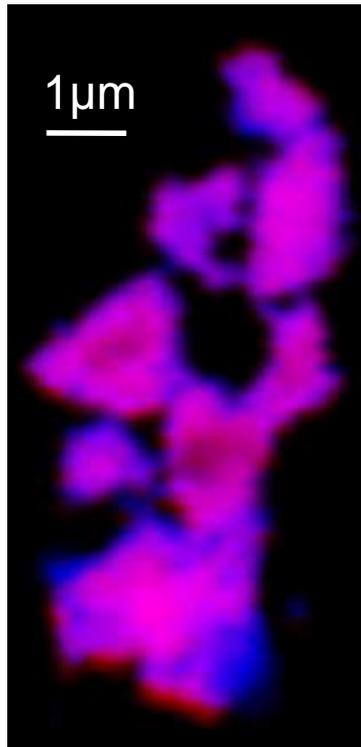
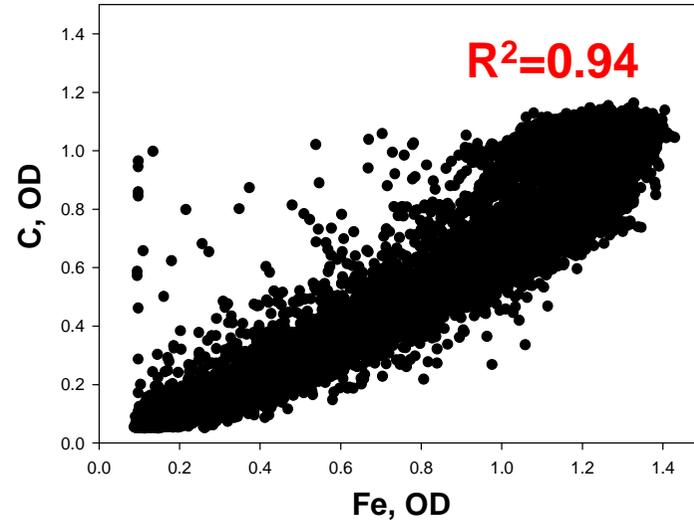
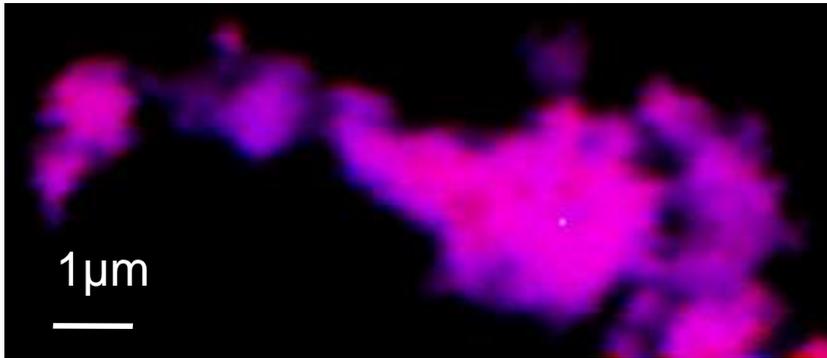
OM-Fe(III) complexes are formed at higher C loadings for coprecipitation.

Fe EXAFS Spectra of the Coprecipitates Formed in the Presence of Organic Matter

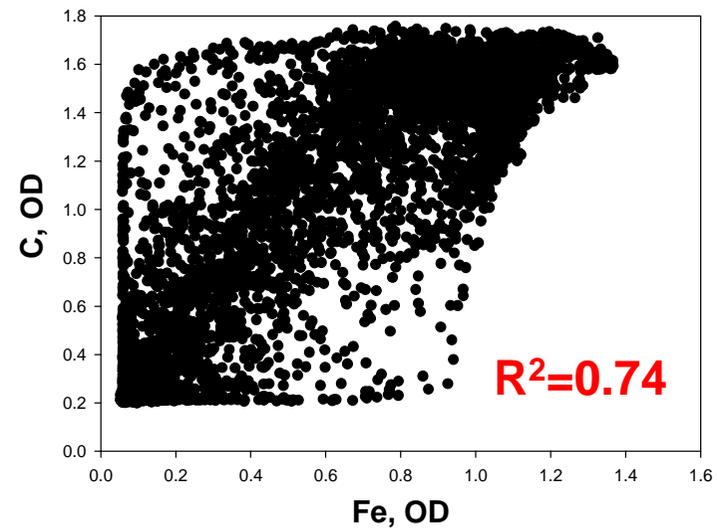


C Distribution on Ferrihydrite via Adsorption

0.52 mg C m⁻² SA



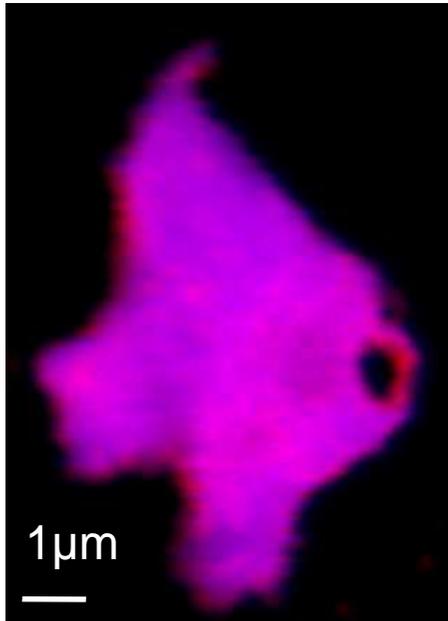
1.30 mg C m⁻² SA



C, Fe

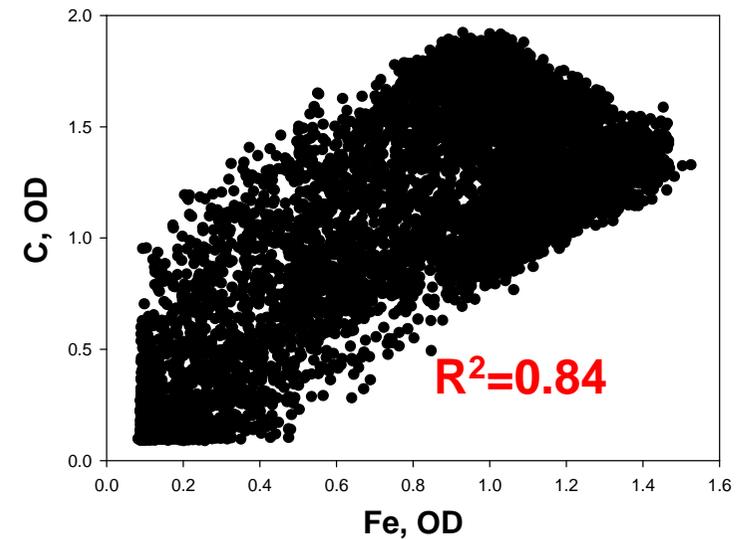
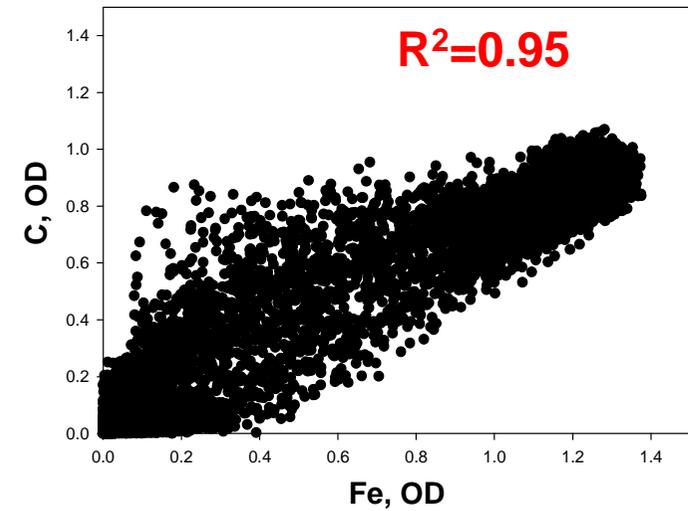
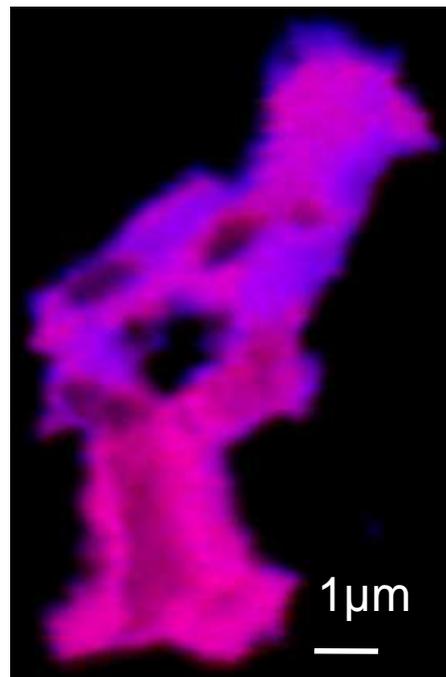
C Distribution on Ferrihydrite via Coprecipitation

0.52 mg C m⁻² SA



C, Fe

1.30 mg C m⁻² SA



Conclusions

- Coprecipitation results in greater C retention and stability than adsorption.
- Organic matter is more stabilized by mineral surfaces and small mineral pores at lower loadings.
- Ligand exchange between carboxylic C and ferrihydrite could be a major mechanism for OM-ferrihydrite interactions for both adsorption and coprecipitation.
- Organic matter-Fe(III) complexes are formed via coprecipitation

Acknowledgements



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Delaware Environmental Institute



Canadian Light Source



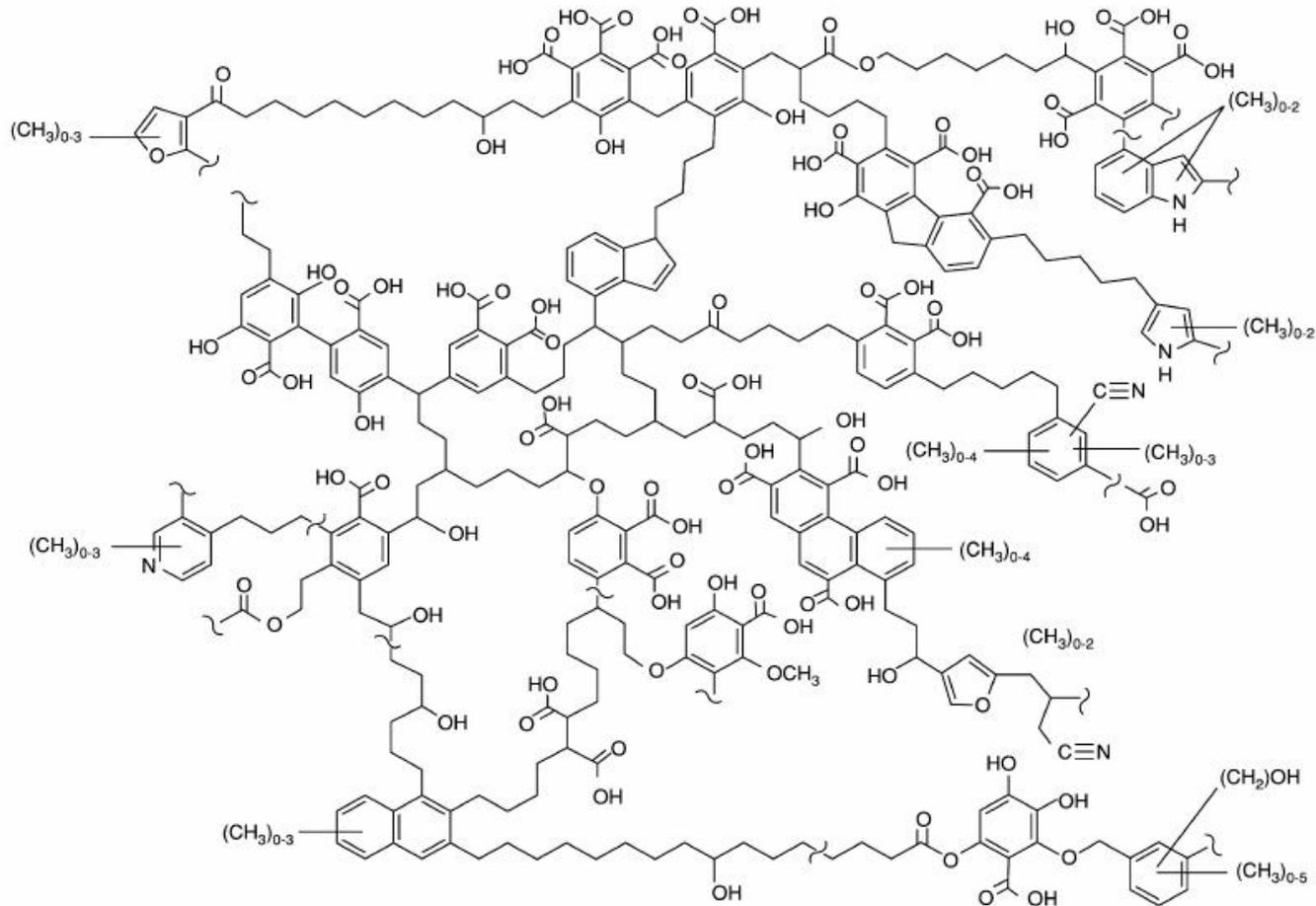
Environmental Molecular Sciences Laboratory



Stanford Synchrotron Radiation Lightsource

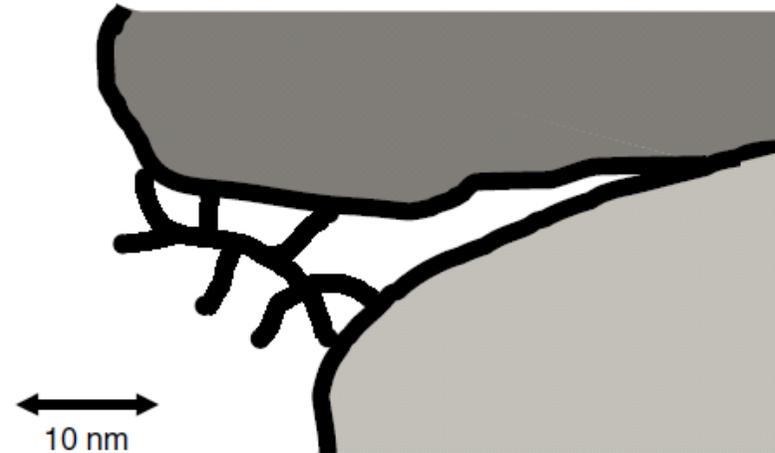
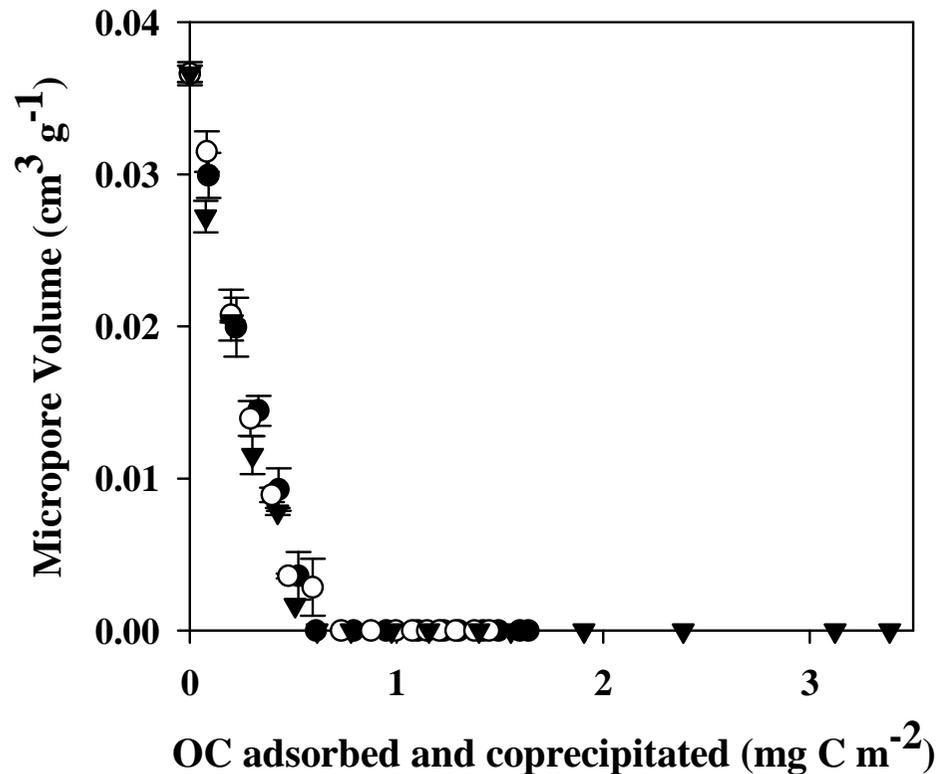


Soil Organic Compounds



- What C functional groups are involved with C-mineral interactions?
- How are the C functional groups spatially distributed on mineral surfaces?

Changes in Micropore (<2 nm) Volume for OM-Ferrihydrite Complexes

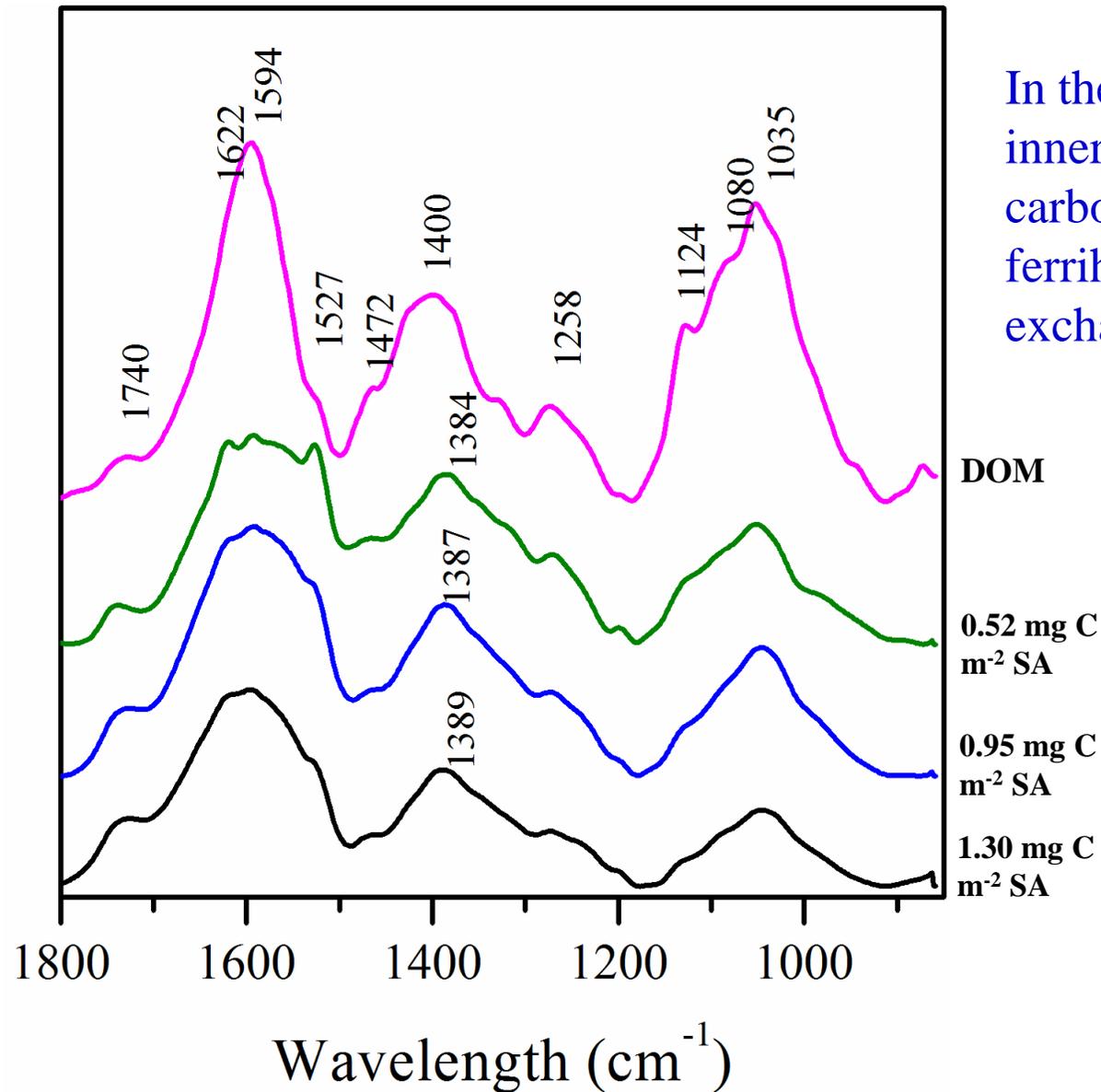


Kaiser and Guggenberger, 2003

Adsorbed or coprecipitated C at the openings of micropores clogged and rendered them inaccessible to N₂

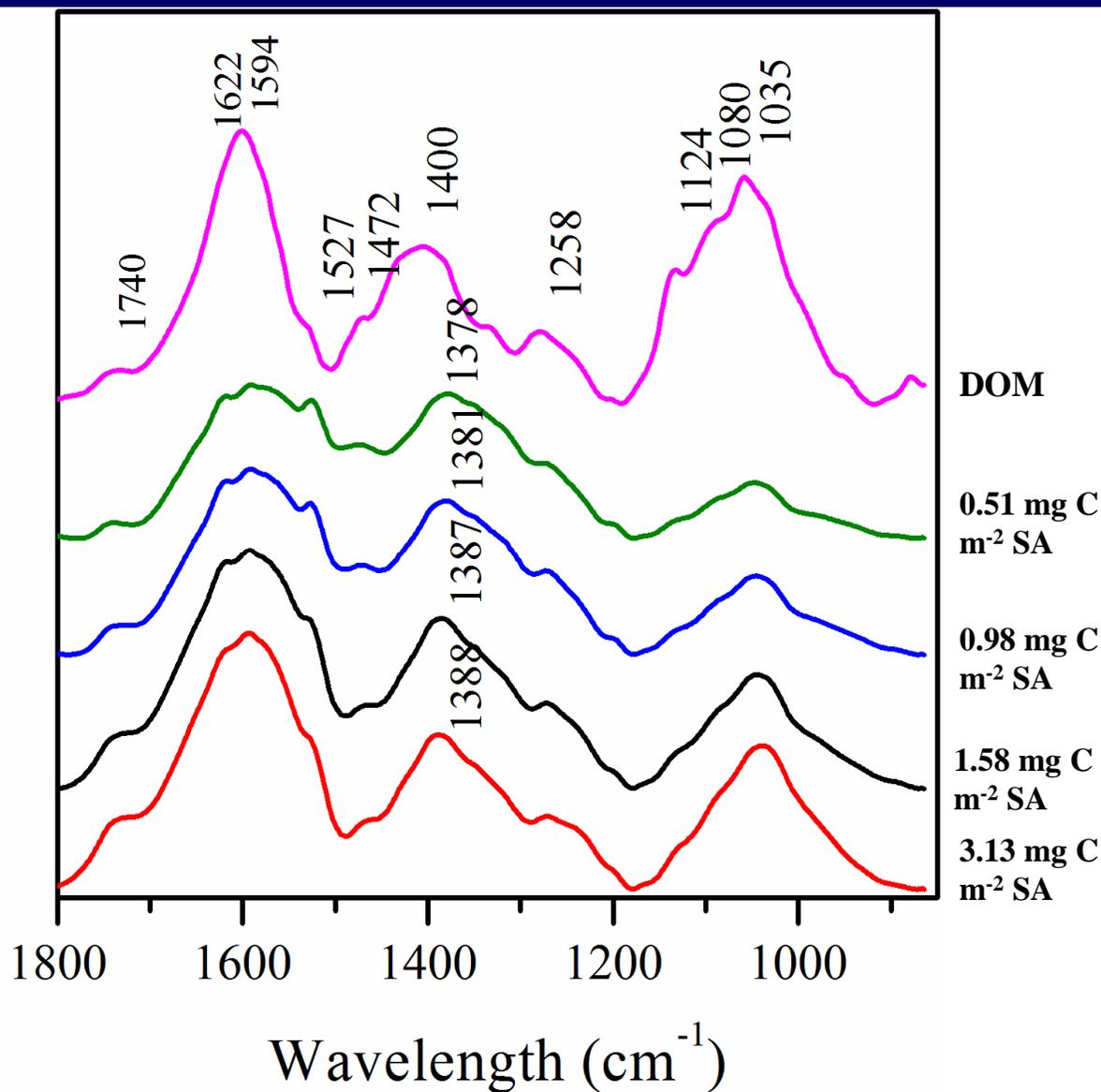
Adsorbed and coprecipitated C led to complete loss of N₂-accessible micropores, indicating micropores are important for carbon-mineral interaction.

FTIR Spectra of the Adsorbed C



In the process of adsorption, strong inner-sphere complexes of carboxylic C groups with ferrihydrite are formed via ligand exchange mechanism.

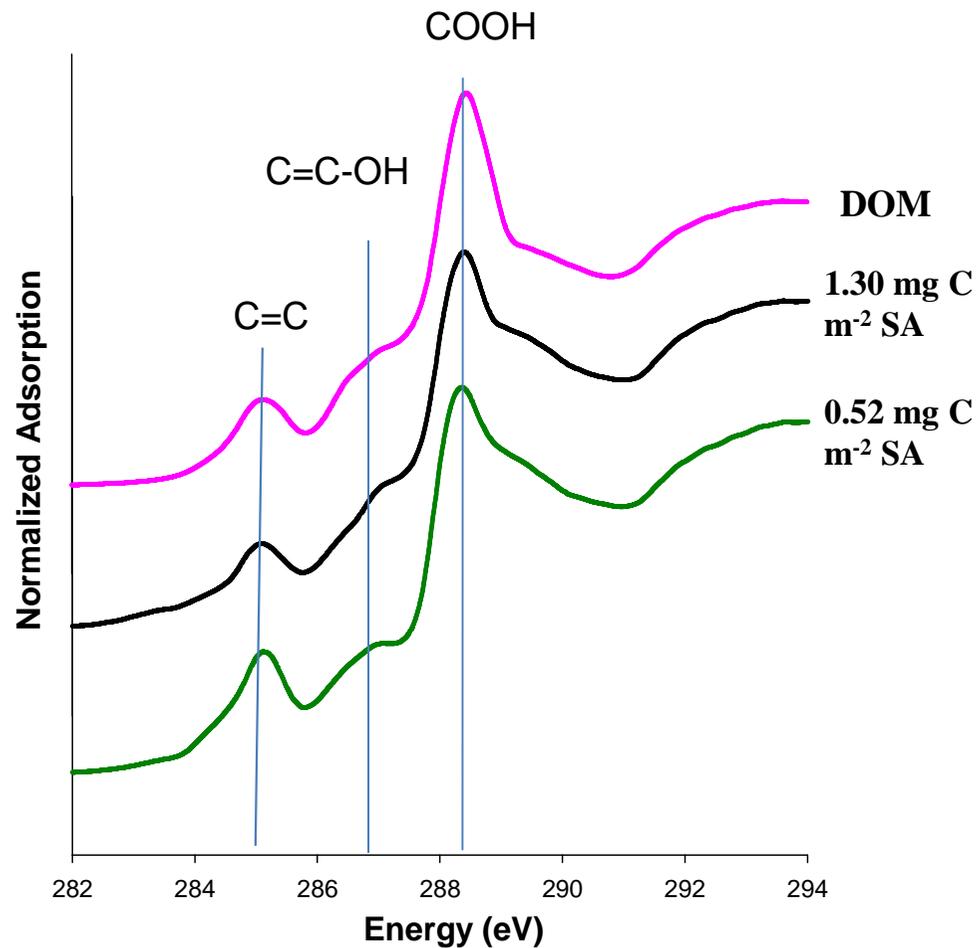
FTIR Spectra of the Coprecipitated C



As adsorption, strong inner-sphere complexes of carboxylic C groups with ferrihydrite are also formed via ligand exchange mechanism for coprecipitation .

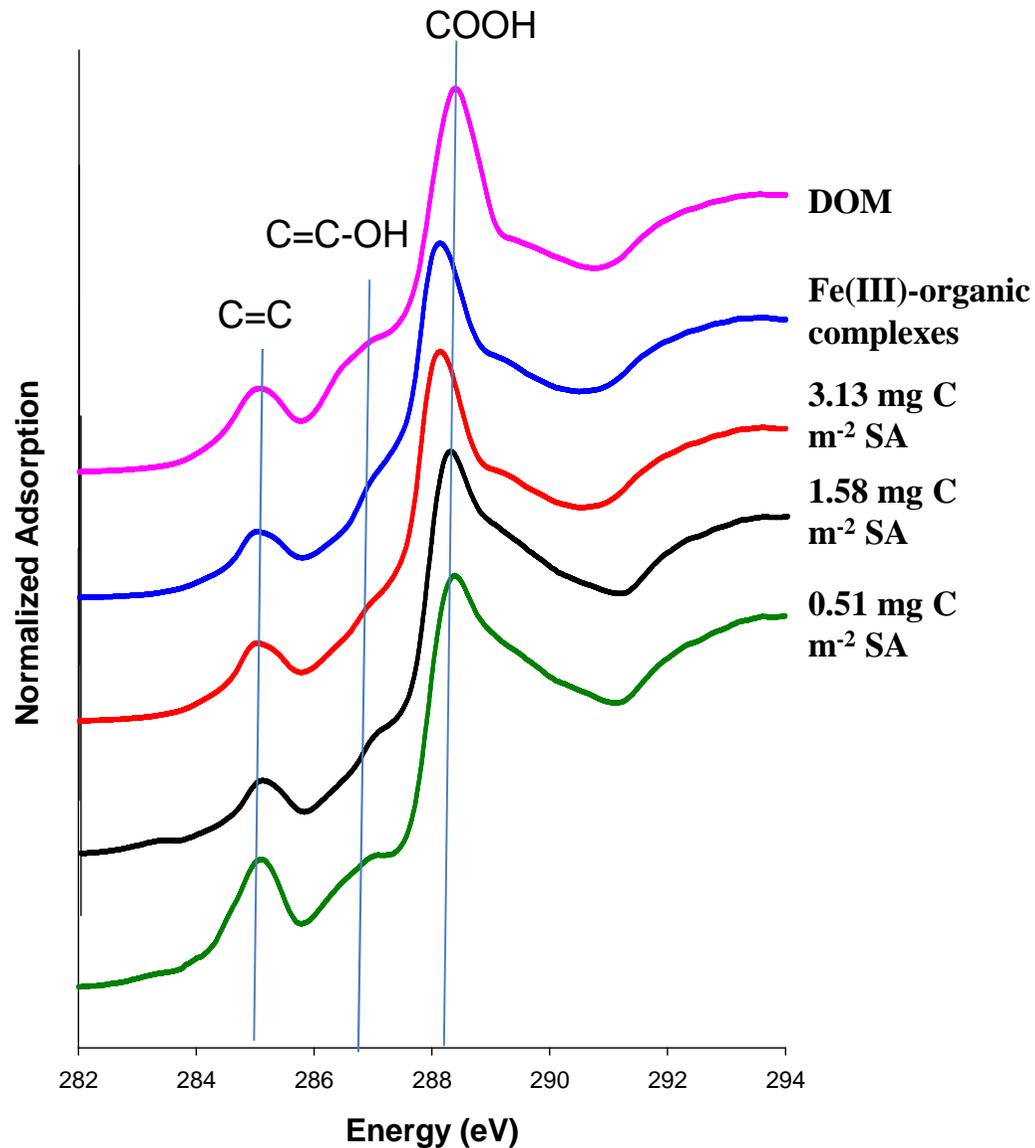
Stronger bonding of Fe-carboxyl C complexes for coprecipitation than for adsorption.

NEXAFS Spectra of the Adsorbed C



Ligand exchange between carboxyl C and ferrihydrite is likely the major mechanism for organo-ferrihydrite interactions.

NEXAFS Spectra of the Adsorbed C



Ligand exchange between carboxyl C and ferrihydrite is likely the major mechanism for organo-ferrihydrite interactions.

Fe(III)-organic complexes are formed at higher C loadings for coprecipitation

Distribution of C forms on Ferrihydrite via Adsorption by STXM

0.52 mg C m⁻²

