



# Stabilization of Soil Organic Carbon

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# Rationale

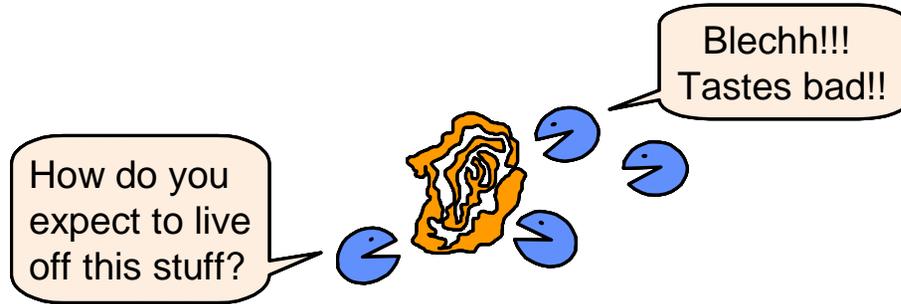
- ⇒ Soil organic C stocks depend on the balance between C inputs and outputs
- ⇒ A soil's capacity to accumulate and store C is greatly affected by its ability to protect and stabilize organic matter against decomposition
- ⇒ A mechanistic understanding of factors controlling SOC transformations and stabilization is needed to:
  - Optimize management strategies for increasing soil C sequestration
  - Improve our ability to predict soil C sequestration potentials



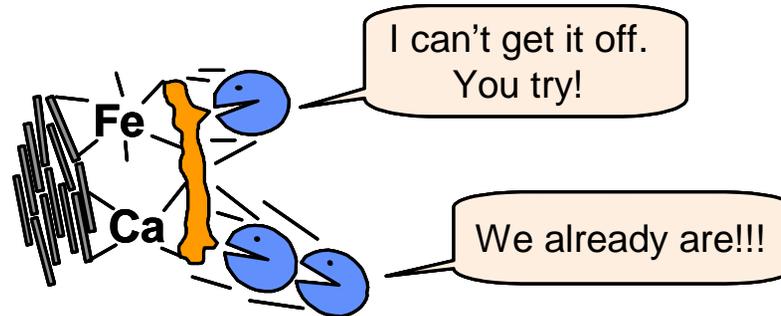
# MECHANISMS OF SOIL ORGANIC MATTER STABILIZATION

From Jastrow and Miller, 1998, *In Soil Processes and the Carbon Cycle*, CRC Press.

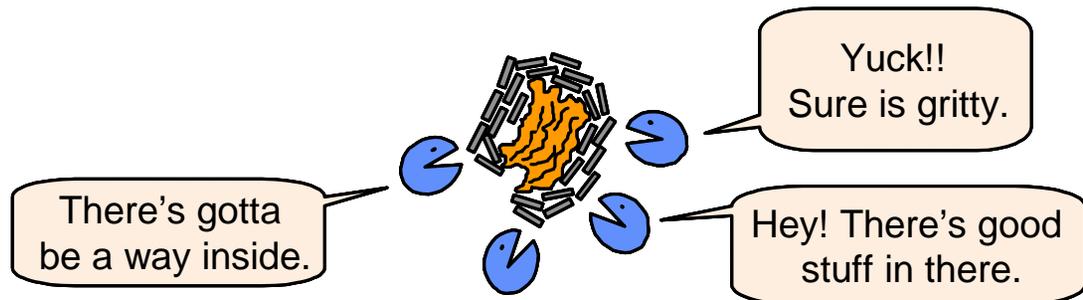
## Biochemical Recalcitrance



## Chemical Stabilization



## Physical Protection





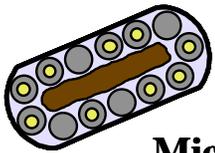
# Objectives

- ⇒ Quantify amounts and dynamics of C and N in soil fractions representing physically and chemically protected SOM pools
- ⇒ Estimate residence times of C in isolated pools
- ⇒ Determine chemical functional composition and structural morphology of selected fractions
- ⇒ Determine extent to which edaphic characteristics, vegetation type, management strategies, and time influence C accumulation in protected pools



# CONCEPTUAL DIAGRAM OF AGGREGATE HIERARCHY

From Jastrow and Miller, 1998, *In Soil Processes and the Carbon Cycle*, CRC Press.



**Microaggregates**

~ 90-250 and 20-90  $\mu\text{m}$



● **Plant and fungal debris**

○ **Silt-sized microaggregates with microbially derived organomineral associations**

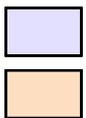
● **Clay microstructures**



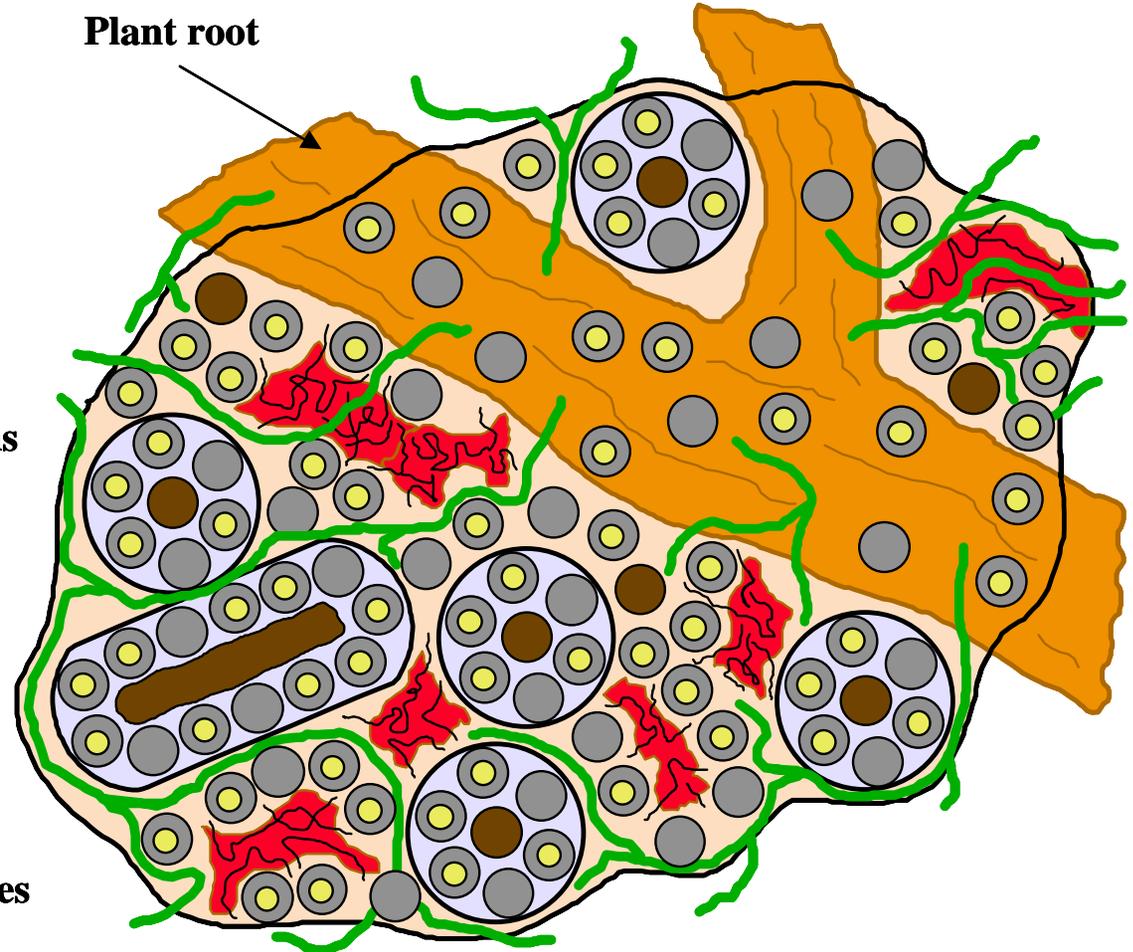
**Particulate organic matter colonized by saprophytic fungi**



**Mycorrhizal hyphae**



**Pore space; polysaccharides and other amorphous interaggregate binding agents**

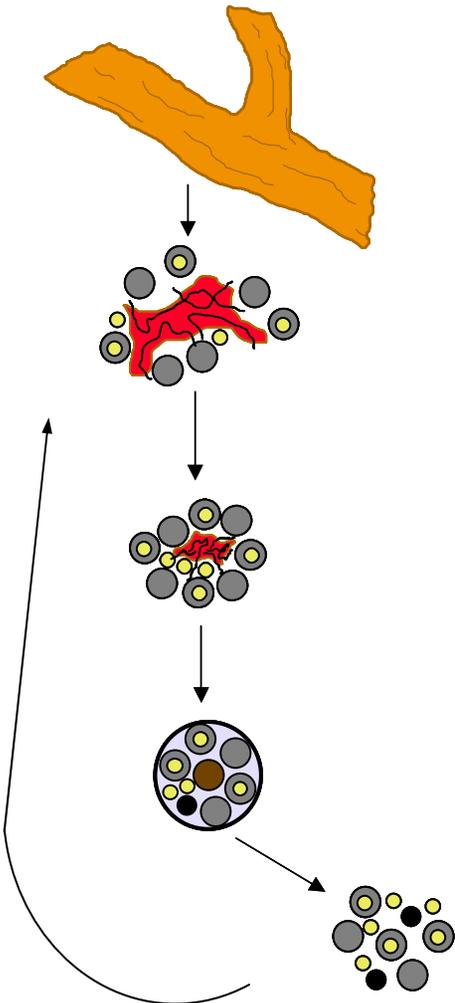
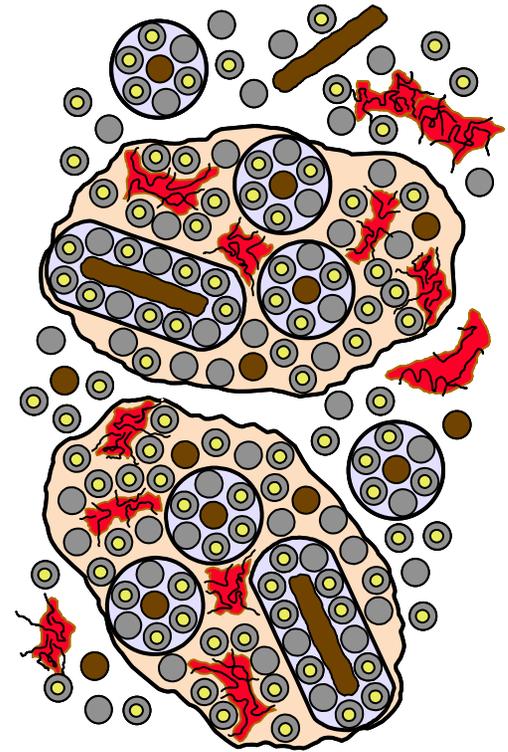




# Conceptual models of soil C cycling and protection mechanisms used to develop new soil fractionations

## Incorporation into microaggregates:

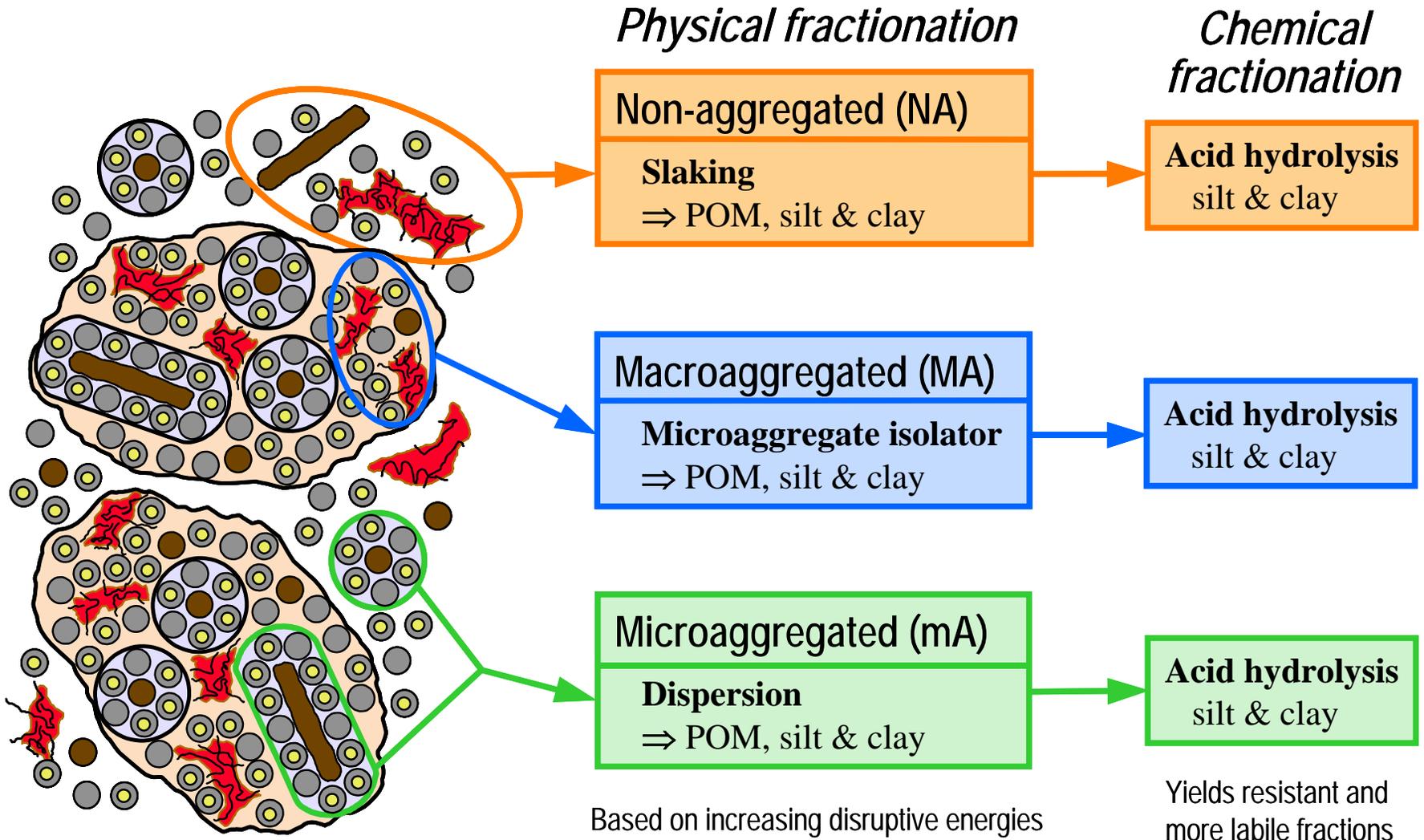
- ⇒ Physically protects organic inputs from decomposition
- ⇒ Enables organic matter to be humified or chemically protected by association with the mineral fraction



	Microaggregates ~ 50-250 $\mu\text{m}$		Plant and fungal debris
	Particulate organic matter colonized by saprophytic fungi		Fungal or microbial metabolites
	Silt-sized aggregates with microbially derived organomineral associations		Biochemically recalcitrant organic matter
			Clay microstructures



# Fractionation of Soil Organic Matter Based on Aggregate Hierarchy





# Evaluating the role that aggregate hierarchy plays in the storage and turnover of soil C

## ⇒ Tracers:

Native Kansas tallgrass prairie dominated by C4 grasses converted to C3 brome grass 62 yr before sampling (fertilized with  $112 \text{ kg N ha}^{-1} \text{ y}^{-1}$ )

## ⇒ Steady state conditions:

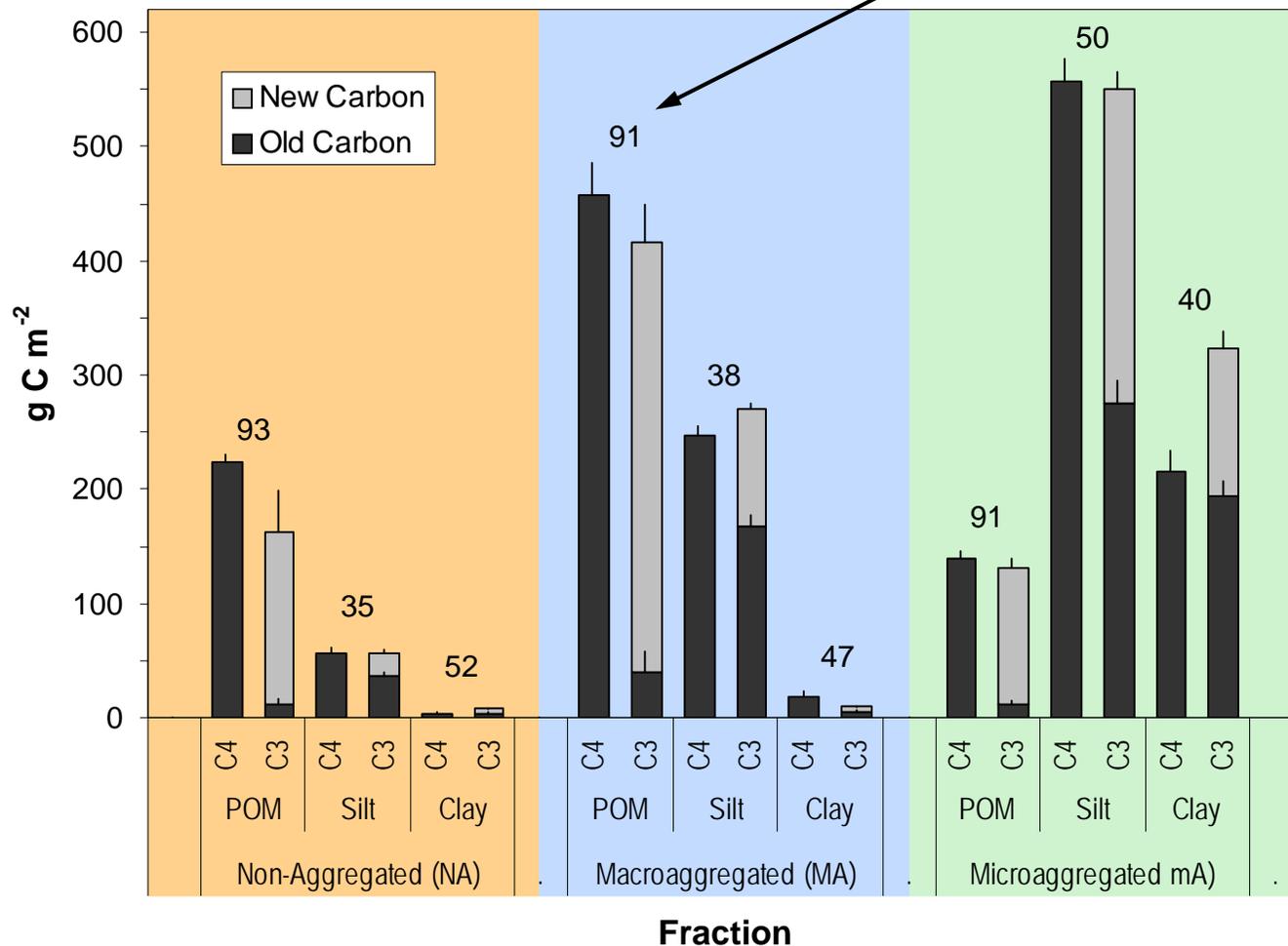
Whole soil C stocks reasonably close to equilibrium

$$\text{C4} = 2028 \pm 25 \text{ g C m}^{-2}$$

$$\text{C3} = 2130 \pm 43 \text{ g C m}^{-2} \quad (\text{surface 5 cm})$$

C4 and C3 axis labels refer to grassland types

Indicates % new C



⇒ Near equilibrium in most fractions

⇒ >55% of POM C in MA (all replaced)

⇒ Most silt and clay C in mA

⇒ No difference in % new C for NA & MA

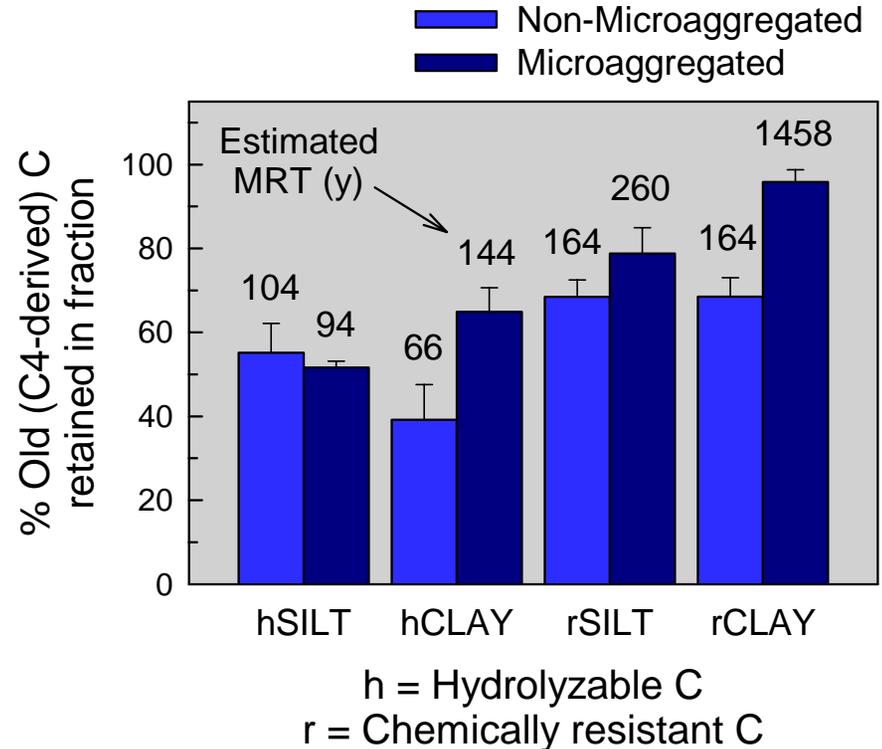
⇒ mA has more new silt C

⇒ mA also has greatest retention of old clay C



# Acid hydrolysis used to evaluate the nature of protected C

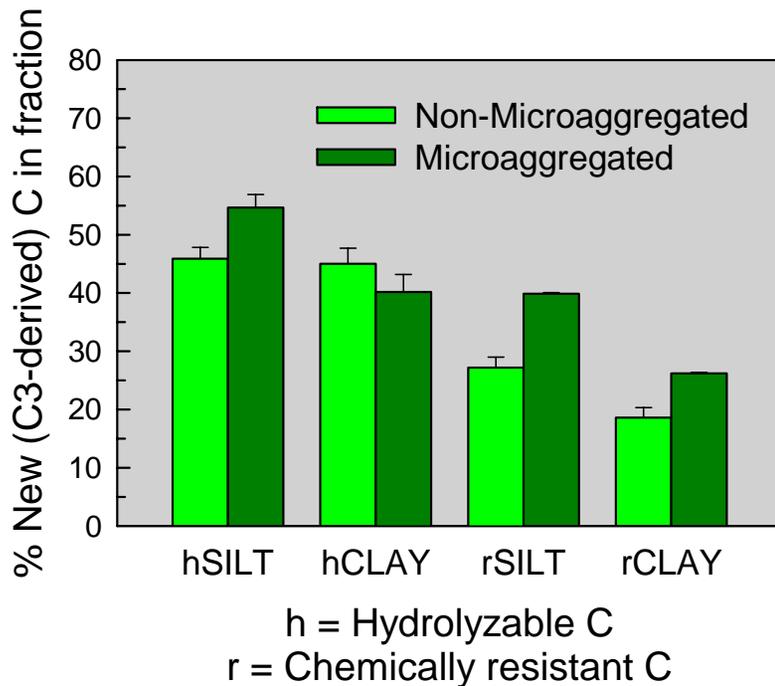
- ⇒ Greater retention of old chemically resistant silt & clay C in microaggregates
- ⇒ Microaggregate protection also increased retention of hydrolyzable clay C



MRT (mean residence time) =  $1/k$ ;  
where  $k$  is estimated as  $-\ln(\% \text{ old C}/100)/62 \text{ y}$



# Acid hydrolysis used to evaluate the nature of protected C

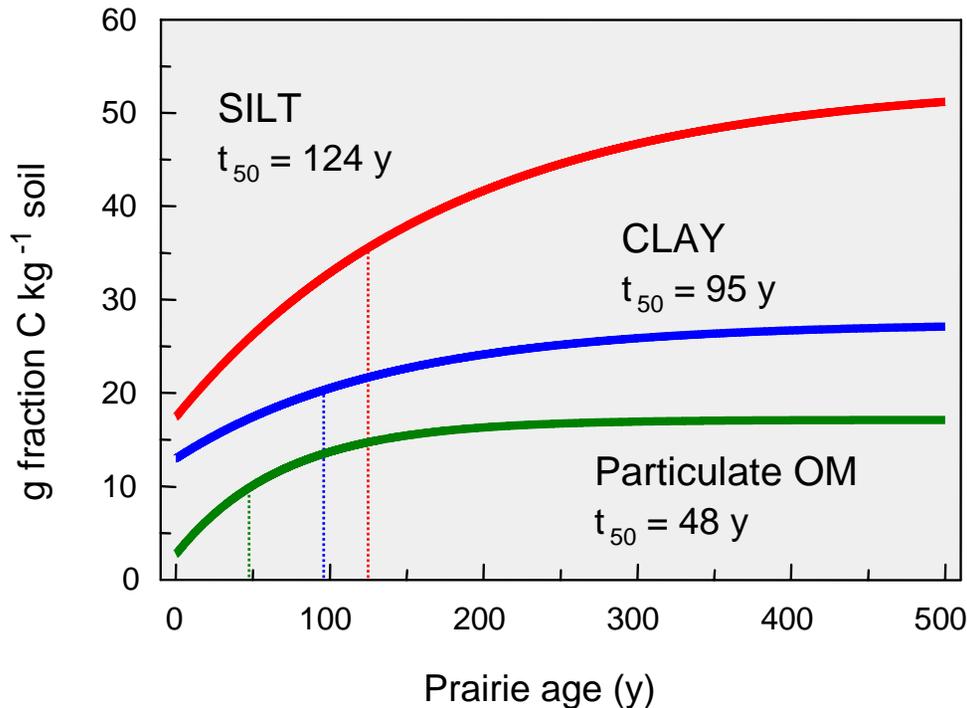


- ⇒ More new chemically resistant C in microaggregated silt & clay
- ⇒ Increased hydrolyzable C in microaggregated silt may be physically protected
- ⇒ Suggests microaggregates can facilitate creation of new organomineral associations

Accumulation of new C in microaggregates suggests these fractions may not be saturated and could increase, even in some high C soils



# Rates of C accrual in soil fractions and their potential saturation limits



## Fermilab Prairie

- ⇒ POM reaches equilibrium first
- ⇒ Clay equilibrates next
- ⇒ Largest increases in silt-sized fraction
- ⇒ ~50% of silt-associated C is chemically resistant across the chronosequence

- ⇒ Aggrading system facilitates investigation of saturation limits
- ⇒ What is the nature and source of accrued C?
  - C4 vs. C3; grass vs. forb; plant vs. microbial; extent of rendering



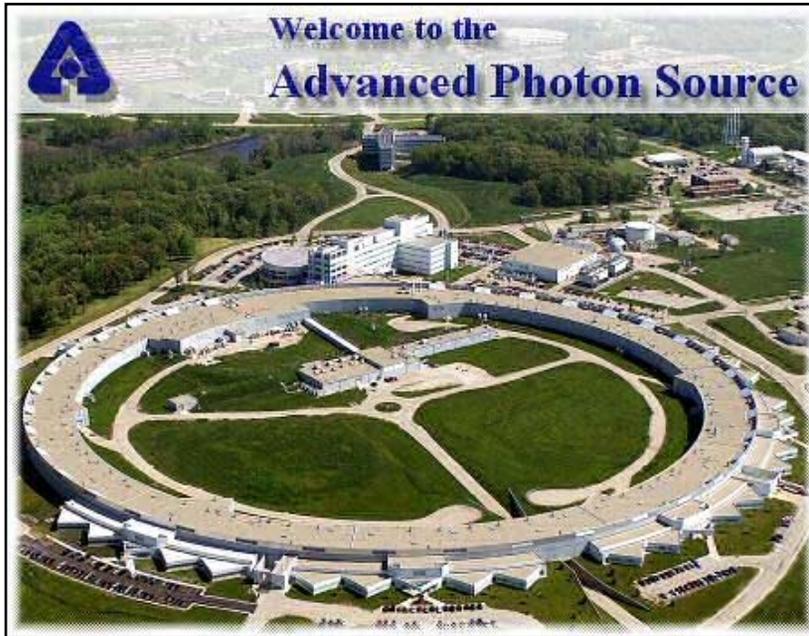
# Organic matter preservation in microaggregates

## Objectives

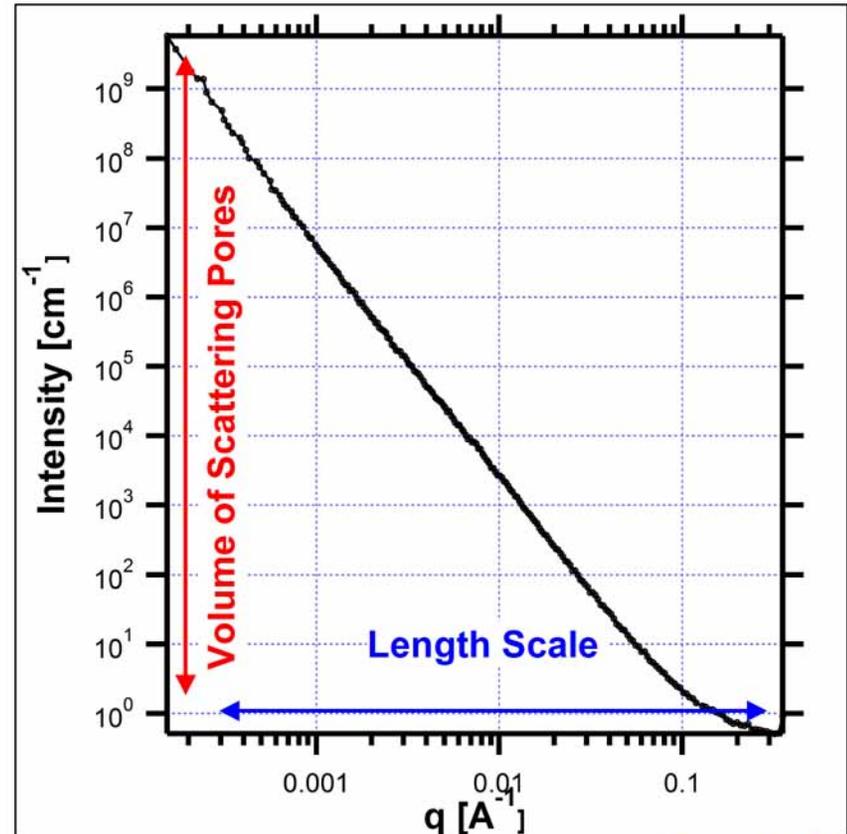
- ⇒ Quantify internal pore structure (*nm to  $\mu\text{m}$* )
- ⇒ Determine location of OM within those pores
- ⇒ Evaluate the role of pore-OM relationships under management practices that increase SOM storage



# Ultra-Small Angle X-Ray Scattering



## USAXS Scattering Curve



- ⇒ Size distribution of pore volume
- ⇒ Quantifies pore sizes ranging from 4 nm to 5  $\mu$ m
- ⇒ Based on change in x-ray contrast
  - Air: *very weak x-ray scatterer*
  - Minerals or OM: *strong scatterers*



# Total and OM-filled porosity by USAXS

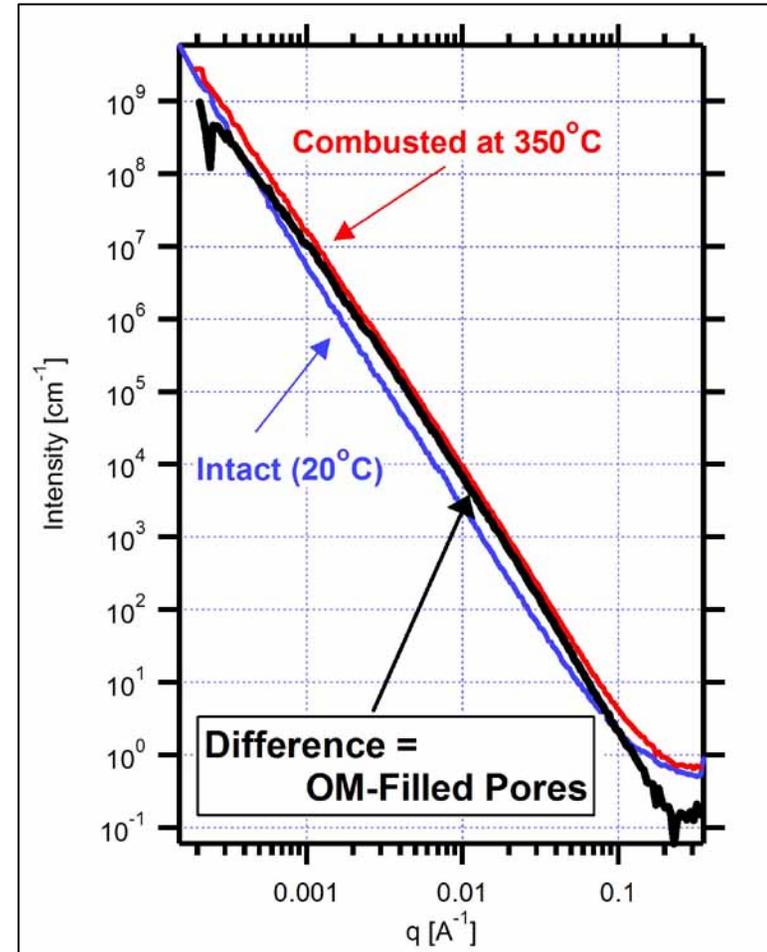
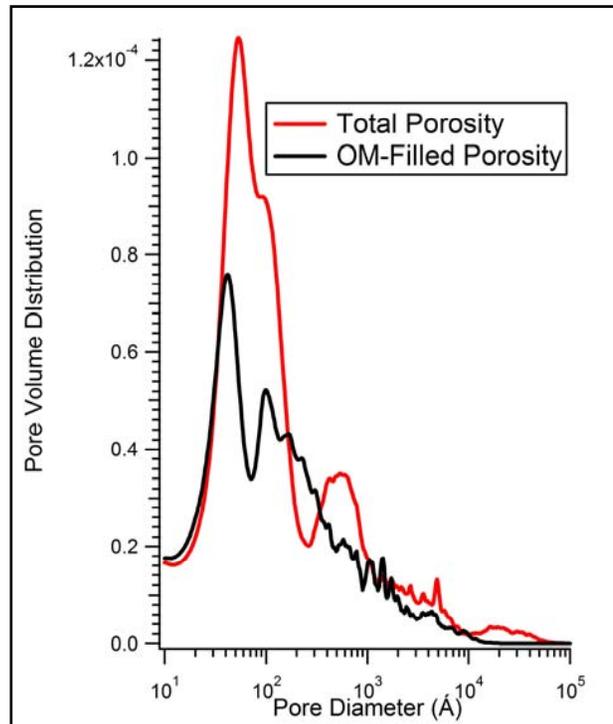
## ⇒ Total Porosity

- Remove OM by combustion

## ⇒ OM-Filled Porosity

- By difference between combusted soil and intact (non-combusted) soil

**Pore Volume Size Distribution**  
(fit from scattering curve)



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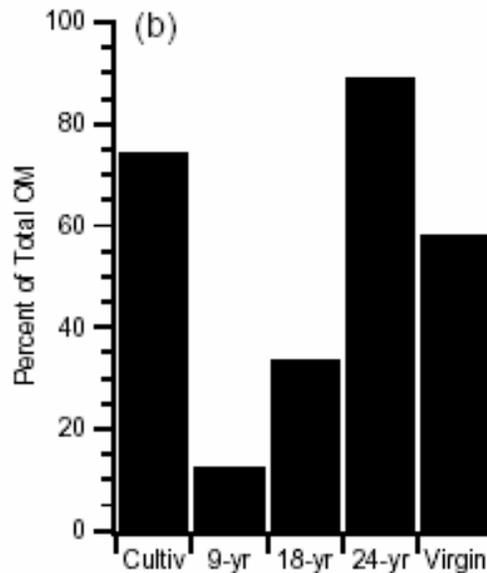




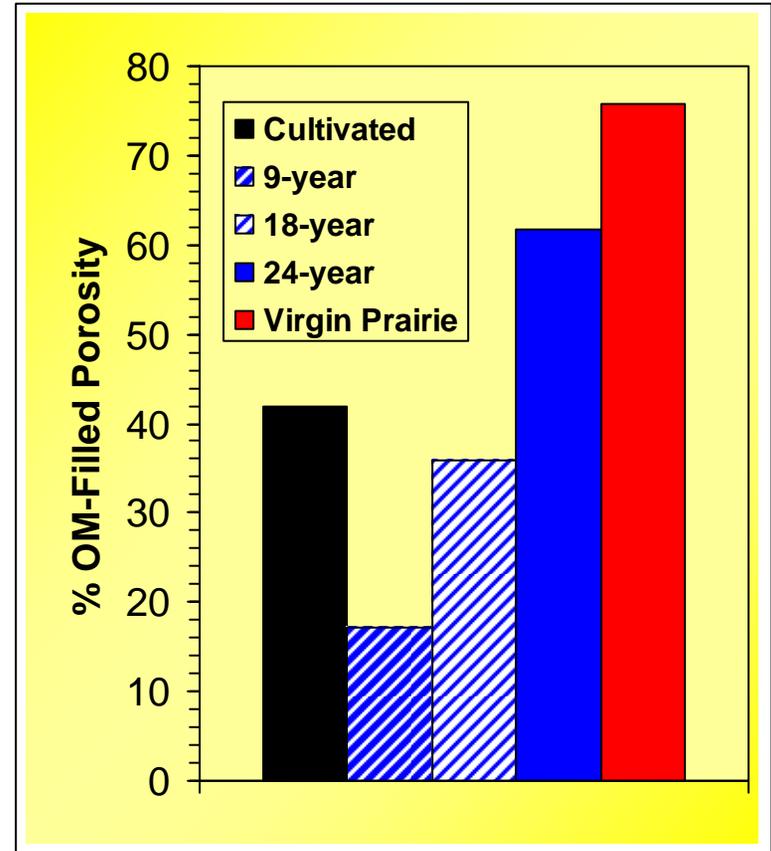
# OM-filled porosity of microaggregates increases with prairie restoration

## Restructuring of OM distribution within pores (<5µm)

- ⇒ Initial loss of OM-filled porosity
  - But cultivated soil has less total pore volume
- ⇒ OM-filled porosity then increases
  - Up to 80% of pores filled with OM
- ⇒ Distribution of total OM within microaggregates also changes, suggesting differences in nature and/or mechanisms protecting OM



## Percent of total pores filled with OM



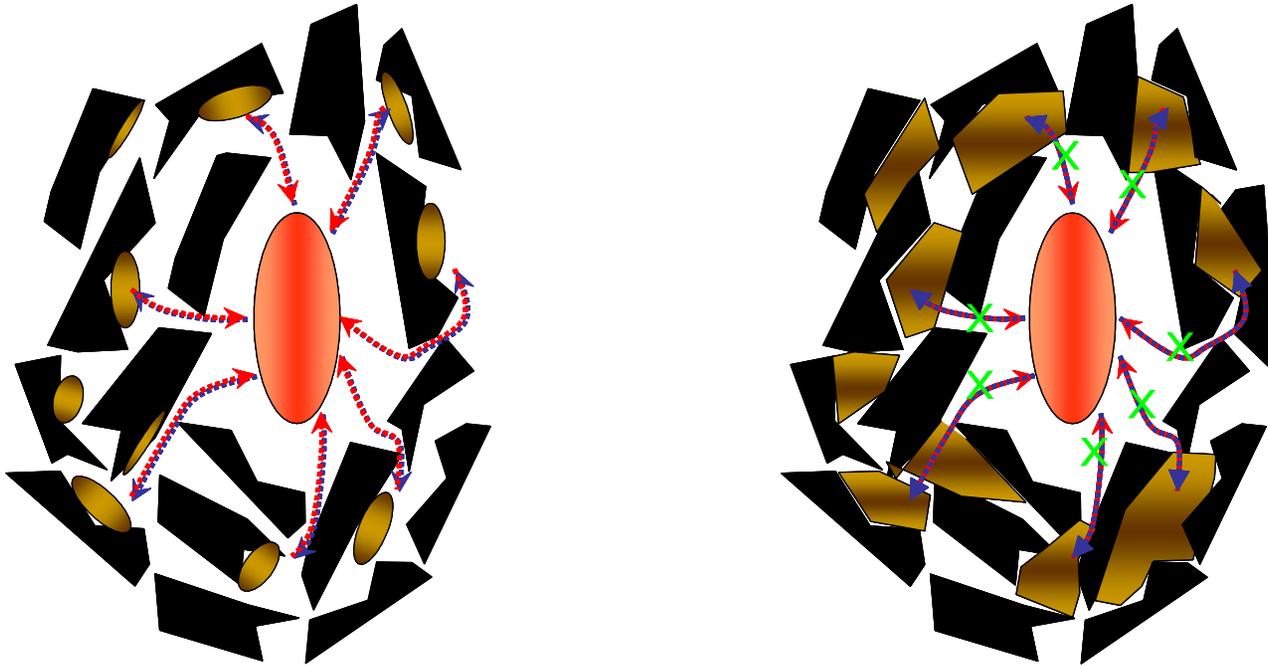
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# Conceptual model of OM protection by OM-filled pores



- ⇒ Slow diffusion of exoenzymes and hydrolyzate
- ⇒ Limit access to OM
  - Only the small surface area at pore necks are accessible
  - OM in pore body is protected
- ⇒ Microbial growth and activity becomes limited



# Microbial enzyme activity and carbon cycling in grassland soil fractions

- ⇒ How do enzymes change across restoration chronosequence?
- ⇒ How do enzymes interact with soil structure to control C balance?
  - Does soil aggregation prevent microbes and enzymes from accessing substrates within aggregates (2° organomineral complexes)?
  - Does enzyme activity reflect the level of degradation and turnover of substrates in 1° organomineral complexes (particle size fractions)?



# Methods

- ⇒ Row crop, 11-yr & 25-yr restored prairie, prairie remnant, and 32-yr C3 grassland
- ⇒ Soil fractions (field-moist bulk soil sieved to 8 mm)
  - Macroaggregates(>250 $\mu$ m): wet-sieving; removed nonaggregated LF with Ludox (1.3 g cm<sup>-3</sup>)
  - Microaggregates: microaggregate isolator (modified from Six et al., 2000)
  - “Primary” particles: coarse (>250 $\mu$ m) & fine (53-250 $\mu$ m) POM, silt- and clay-sized fractions (dispersion in water 60 min on wrist-action shaker with glass beads)
- ⇒ Potential enzyme activity of fractions and bulk soil assayed (modified from Sinsabaugh et al., 1993)
  - Enzyme recovery from POM, silt & clay fractions was 84-112% of bulk soil



# Assayed enzymes and their functions

Enzyme	Function
Phosphatase	Releases $\text{PO}_4^{3-}$
Protease	Releases amino acids
Chitinase	Releases chitin monomers
Beta-glucosidase	Degrades cellulose
Cellobiohydrolase	Degrades cellulose
Polyphenol oxidase	Degrades lignin

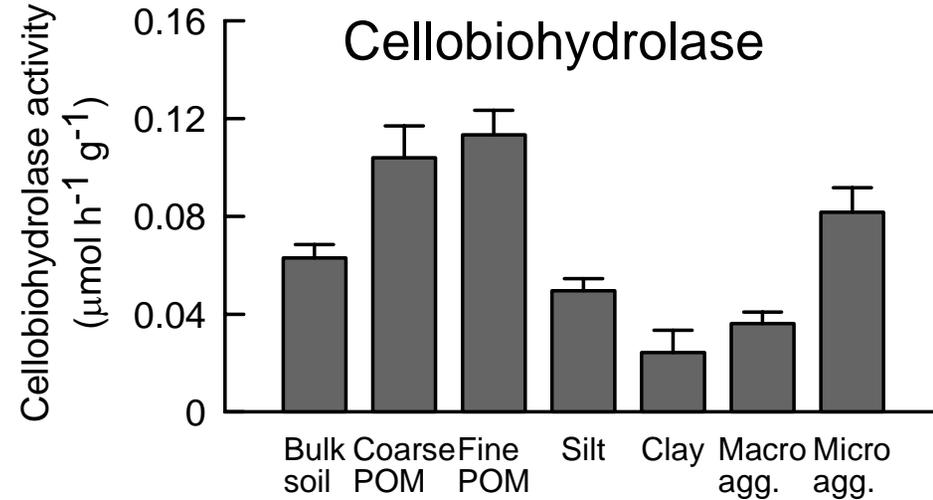
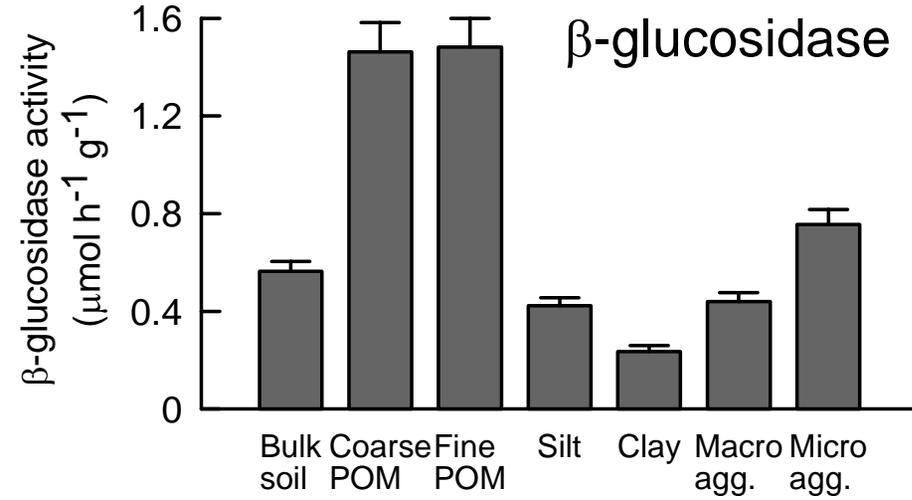


# Predictions

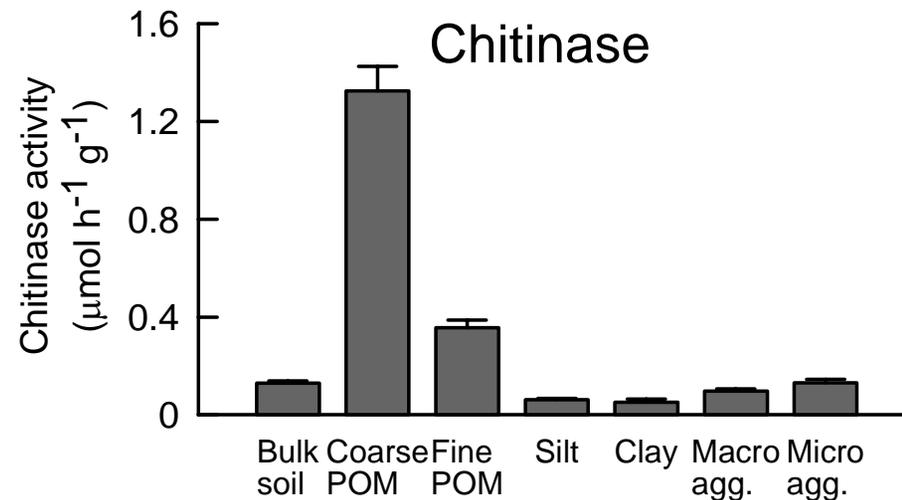
<b>Fraction (Estimated MRT of C)</b>	<b>Prediction</b>
<b>Particulate organic matter (6-30 yr)</b>	<b>Accessible substrates, high microbial activity; high enzyme activity</b>
<b>Macroaggregates (50 yr)</b>	<b>Includes coarse particulate organic matter; above average enzyme activity</b>
<b>Microaggregates (80 yr)</b>	<b>Physically protected; below-average enzyme activity</b>
<b>Silt (75 yr)</b>	<b>Low enzyme activity</b>
<b>Clay (200 yr)</b>	<b>Lowest enzyme activity</b>



# Cellulose- and chitin-degrading enzymes localized near their substrates

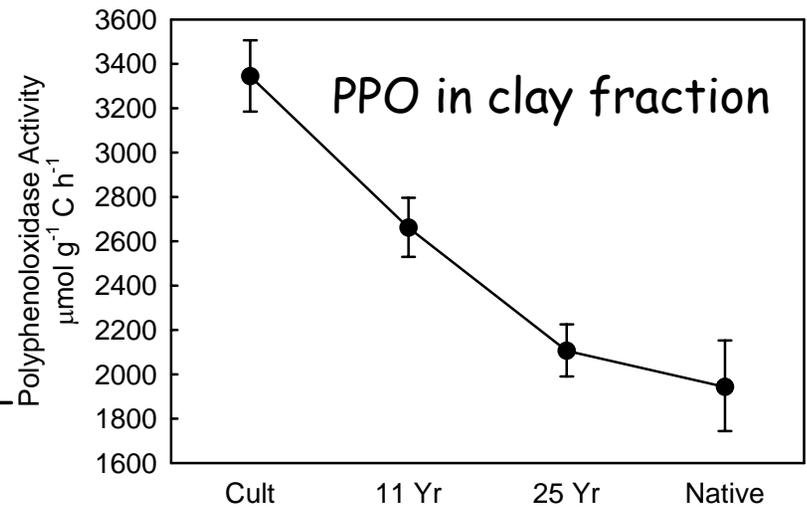
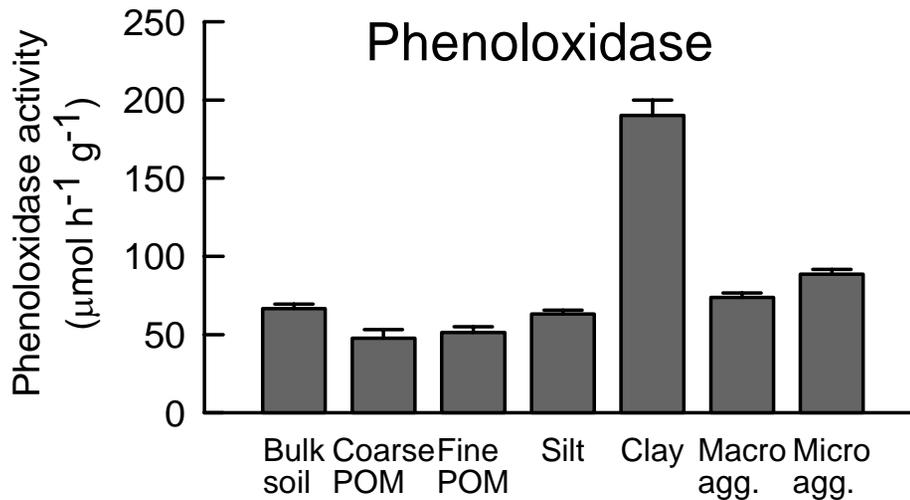


- ⇒ Changes across the chronosequence were small relative to fraction differences
- ⇒ General increase in activity was related to increase in C content





# Polyphenoloxidase localized in clay fraction

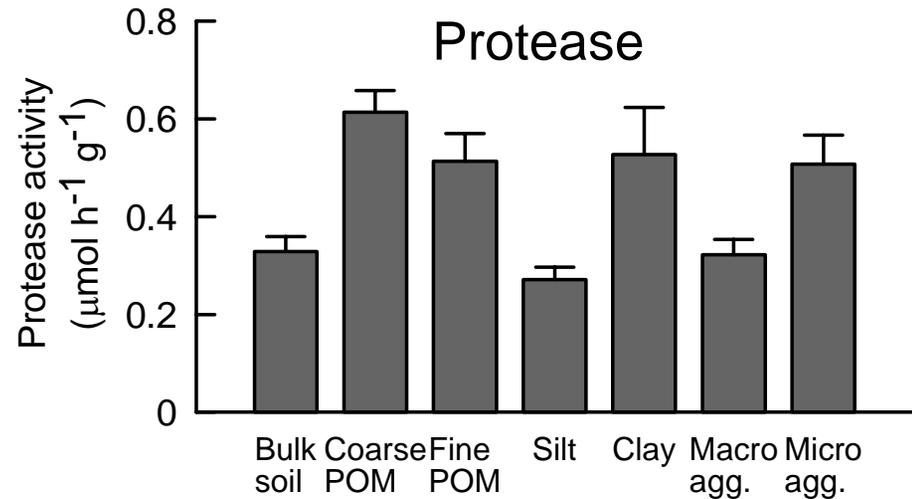
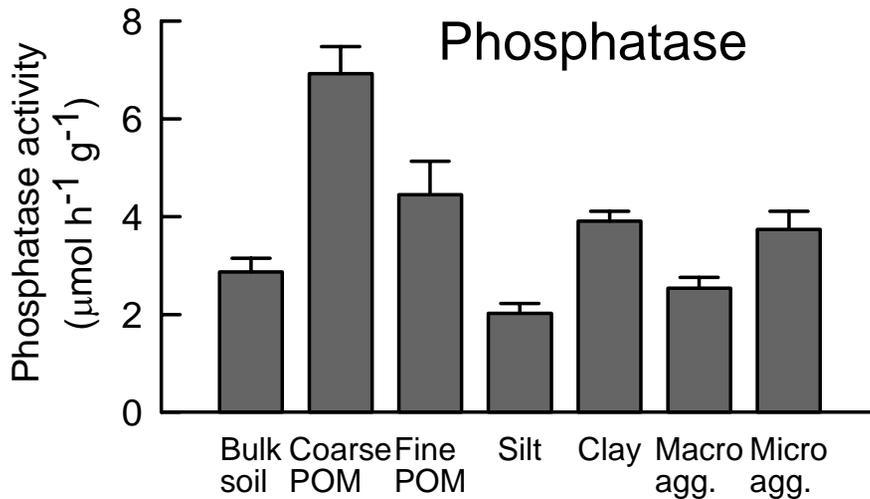


Phenoloxidase relatively constant with soil mass but declines by almost 50% across chronosequence

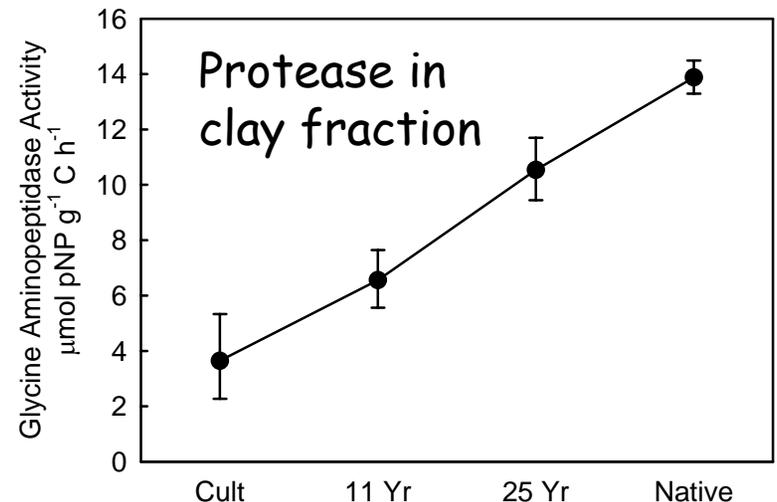
- ⇒ Suggests enzymes are bound to minerals independent of substrate concentrations
- ⇒ OR excluded from access to substrates in OM-filled pores



# Nutrient enzymes produced across all fractions relative to SOM contents



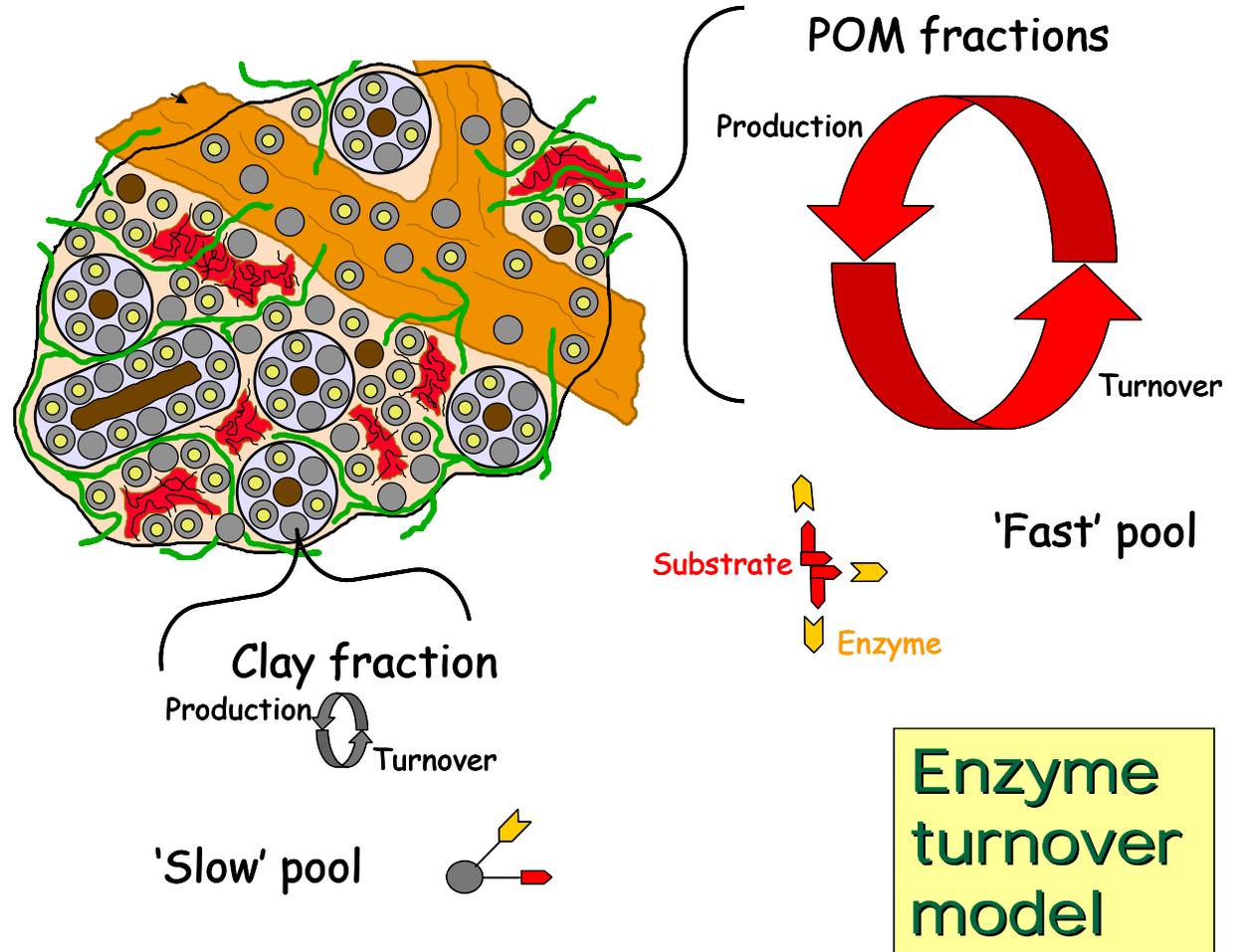
- ➡ Protease activity more than triples relative to C content in clay
- ➡ Likely tied to organic sources of N in accumulating peptides and amino compounds





# Conclusions

- ⇒ High production of specific enzymes on organic substrates
- ⇒ Specific locations of enzymes unresolved: inside aggregates or on aggregate surfaces?
- ⇒ Substantial potential activity in C fractions with long mean residence times
- ⇒ 'Two pool' model of enzyme activity?





# Significance and goals

- ⇒ Gain better mechanistic understanding of factors controlling long-term C stabilization in soils
- ⇒ Determine how management practices and site factors (e.g., soil type, climate) affect:
  - C inputs to pools with varying residence times
  - Potential for long-term C storage in protected pools
- ⇒ Contribute to better parameterization or refinement of existing models and/or development of a new generation of SOM models based on measurable pools