Fe(II)-catalyzed transformation of Fe (hydr)oxides in particle-size soil organic matter from amended agricultural soils
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Which are the effects of organic matter on the extent and pathway of Fe$^{2+}$-catalyzed transformation? 
The Fe$^{2+}$-catalyzed transformation is an unexplored pathway for C mobilization or sequestration.
HYPOTHESIS:
Soil organic matter (SOM) quantity, quality, and distribution between different pools can affect Fe(III) oxides transformation under reducing conditions by altering Fe atom exchange kinetics.

MAIN OBJECTIVES:
• To determine the effect of organic amendments on the Fe(II)-induced abiotic transformation of Fe(III) minerals in an agricultural soil (simulated temporary anoxia).

• To investigate the influence of Fe-OM associations on mineral transformations across particle-size SOM pools.
Fe speciation in SOM pools under agricultural soils subjected to biochar and organic fertilizers amendments.

- Unamended agricultural soil (UN).
- Municipal solid waste amended soil (MC).
- Biochar amended soil (BC).
- Biochar and municipal solid waste amended soil (BC+MC).
- Bulk, fine sand (FSa) and fine silt plus clay (FSi+Cl) fractions.

Plaza et al. 2016

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04 Physical Fractionation

SOIL SAMPLE
(air-dried, 2mm sieved)

Mechanical sieving
Ultrasonic dispersion

Sieving centrifugation

DISPERSED SOIL

Organic fragments
2000-200 μm

Organic fragments
200-50 μm

Organic fragments
50-20 μm

Particulate organic matter
(POM > 20 μm)

Organo-mineral complexes
<20 μm

Lopez-Sangil and Rovira, 2013
Giannetta et al. 2019

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05 Fe(II) SPIKING

physical fractionation

Bulk  FSa  FSi+Cl
**06 Fe SPECIATION: Fe EXAFS**

**Basic Experiment:**

- X-ray beam → Ion chamber detector → Sample → Ion chamber detector

**XANES / NEXAFS**
- Oxidation state, Molecular structure, Electronic structure.

**EXAFS Oscillations**
- Pre-edge
- Edge

**EXAFS**
- Quantitative Local Structure.

- Fe₂O₃
- Fe₂O₃

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### RESULTS: Fe EXAFS Bulk soils

<table>
<thead>
<tr>
<th>Sample</th>
<th>n. components</th>
<th>Component 1</th>
<th>Component 2</th>
<th>Component 3</th>
<th>Component 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>UN</td>
<td>3</td>
<td>CHLORITE</td>
<td>LEPIDOCROCITE</td>
<td>FE(III)-CITRATE</td>
<td></td>
</tr>
<tr>
<td>MC</td>
<td>3 and 4</td>
<td>CHLORITE</td>
<td>LEPIDOCROCITE</td>
<td>FE(III)-CITRATE</td>
<td>FERRIHYDRITE</td>
</tr>
<tr>
<td>BC</td>
<td>3</td>
<td>CHLORITE</td>
<td>LEPIDOCROCITE</td>
<td>FE(III)-CITRATE</td>
<td></td>
</tr>
<tr>
<td>BC+MC</td>
<td>4</td>
<td>CHLORITE</td>
<td>LEPIDOCROCITE</td>
<td>FE(III)-CITRATE</td>
<td>FERRIHYDRITE</td>
</tr>
</tbody>
</table>

- PCA
- TT
- SPOIL
- R-values
- F-test
- LCF

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**RESULTS: Fe(II)-CATALYZED OXIDE TRANSFORMATION IN THE FSi+Cl FRACTION**

- FSi+Cl fraction before Fe(II) addition: 3 components.
- FSi+Cl fraction after Fe(II) addition: 4 components.

Ferrihydrite was transformed to lepidocrocite. The percentage of lepidocrocite remained stable in both the unamended and amended soils.
**RESULTS:** Fe(II)-CATALYZED OXIDE TRANSFORMATION IN THE FSa FRACTION

**FSa**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Chlorite</th>
<th>Lepidocrocite</th>
<th>Fe(III)-Citrate</th>
<th>Ferricyanide</th>
</tr>
</thead>
<tbody>
<tr>
<td>UN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UN + Fe(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC + Fe(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td></td>
<td></td>
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<tr>
<td>BC + Fe(II)</td>
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<tr>
<td>BC + MC</td>
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<td></td>
</tr>
<tr>
<td>BC + MC + Fe(II)</td>
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</tr>
</tbody>
</table>

**UN:** lepidocrocite formation.

**MC:** lepidocrocite formation hindered.

**BC:** biochar functions as an electron shuttle, thus favoring the reduction of the Fe(III) oxyhydroxides.

**BC + MC:** intermediate situation.

**FSa** fractions represent an understudied pool of SOM reactive to Fe mineral transformation.

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SOM quantity, quality and distribution between different pools can affect Fe(III) oxides transformation under reducing conditions by altering Fe atom exchange kinetics.

• The increase in SOM due to organic amendments can contribute to limiting abiotic Fe(II)-catalyzed ferrihydrite transformation.
• This effect of amendment on Fe oxide transformation is less evident in fine with respect to coarse particle-size fractions.
• In this fraction, Fe(II) addition mainly lead to the transformation of ferrihydrite to lepidocrocite, however this depended on organic amendment type.
• With respect to compost, biochar addition favored the formation of both lepidocrocite and magnetite, possibly due to the role of aromatic constituents in electron shuttling.
Thank you for your attention

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