

# Ferrihydrite Transformation in Flooded Rice Paddy Soils with Diffusion Limited Fe(II) Supply

Andrew R. C. Grigg, Katrin Schulz, Katherine A. Rothwell,  
Laurel K. ThomasArrigo, Ruben Kretzschmar

Soil Chemistry Group, Institute of Biogeochemistry and Pollutant Dynamics,  
CHN, Universitätstrasse 16, ETH Zurich, 8092 Zürich, Switzerland  
andrew.grigg@usys.ethz.ch

## Iron minerals:

- are abundant in soils;
- have a major influence on the cycling of trace elements; and
- undergo transformations in redox dynamic soils that have the potential to immobilise or remobilise trace elements [1].

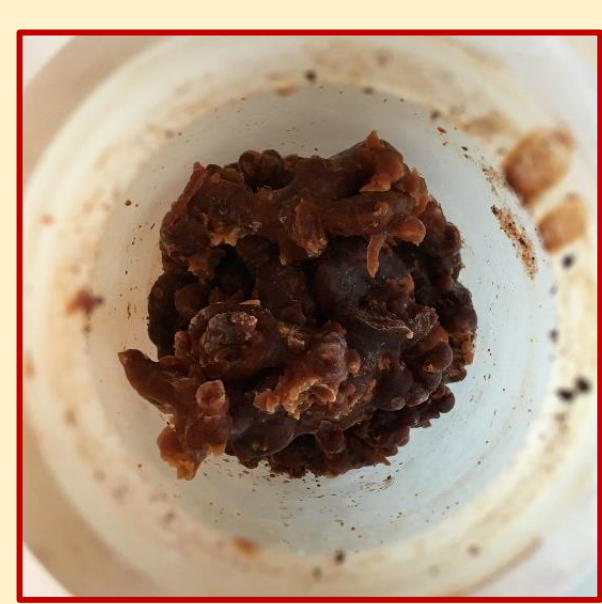
However, the way that complex soil environments influence transformation processes is not currently well understood. Carrying out mineral transformation studies in soils is experimentally challenging.

## In this study:

- We measured ferrihydrite (Fh) transformation using permeable fabric sachets to insert minerals into flooded rice-growing paddy soils from Bangladesh [2], China and Thailand.
- We measured changes in soil pore water composition and related chemical composition to changes in mineral identity.

Ferrihydrite is a short range ordered iron oxyhydroxide. We studied Fh transformation because Fh is a common mineral in redox active soils, and is quickly transformed to other Fe minerals, such as lepidocrocite (Lp) and goethite (Gt) [3].

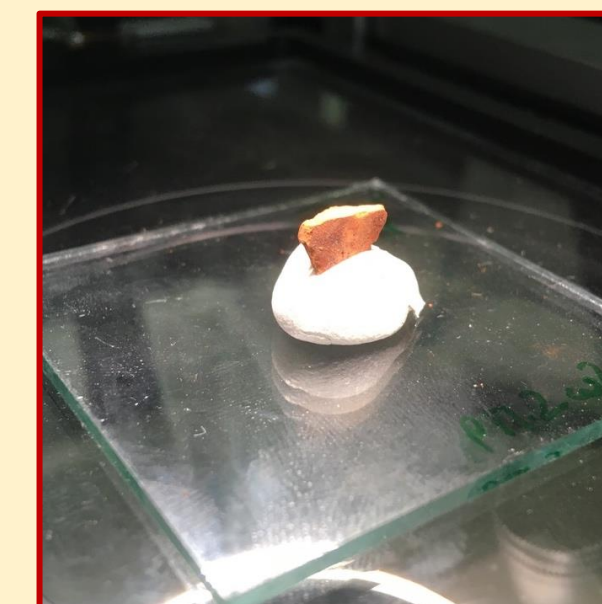
## Methods



1. We synthesised Fh in the laboratory. Porous PETE sachets (dimensions approximately 30 mm × 12 mm × 3 mm, pore size 52 μm) were filled with ~0.5g of Fh.



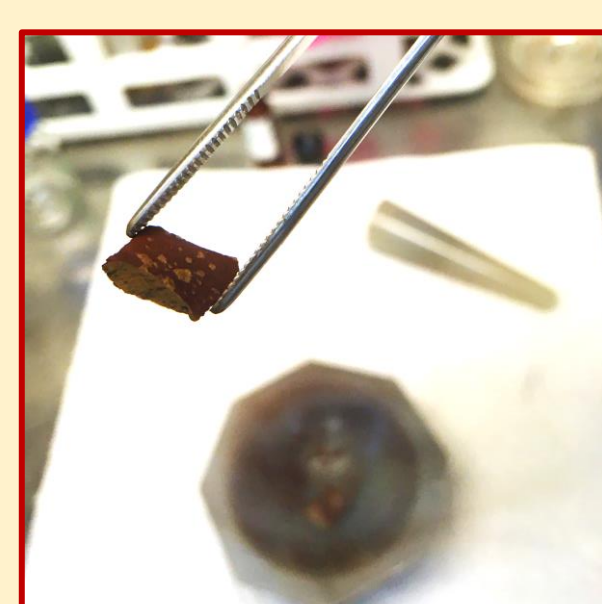
3. After the incubation, pore water was sampled with pre-inserted pore water samplers. Redox potential and pH were measured in-situ.



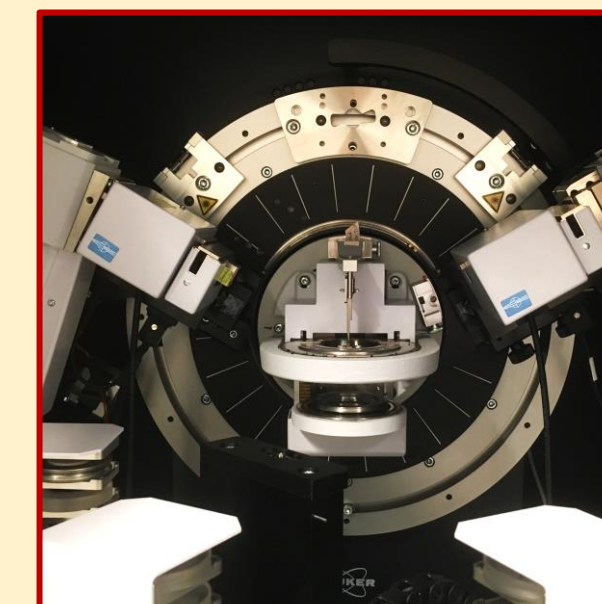
5. Raman spectra (Renishaw InVia Raman microscope) were taken in a grid across each cross-section surface. The share of ferrihydrite (Fh), goethite (Gt) and lepidocrocite (Lp) in each spectrum was determined using component analysis.



2. We buried the sachets, in microcosms of ~300 g of soil flooded for two weeks with 350mL of 5mM CaCl<sub>2</sub>.



4. Mineral sachets removed and air-dried in the glove box. Mineral sachets were cut open and either carefully cross-sectioned and mounted in pieces, or crushed.

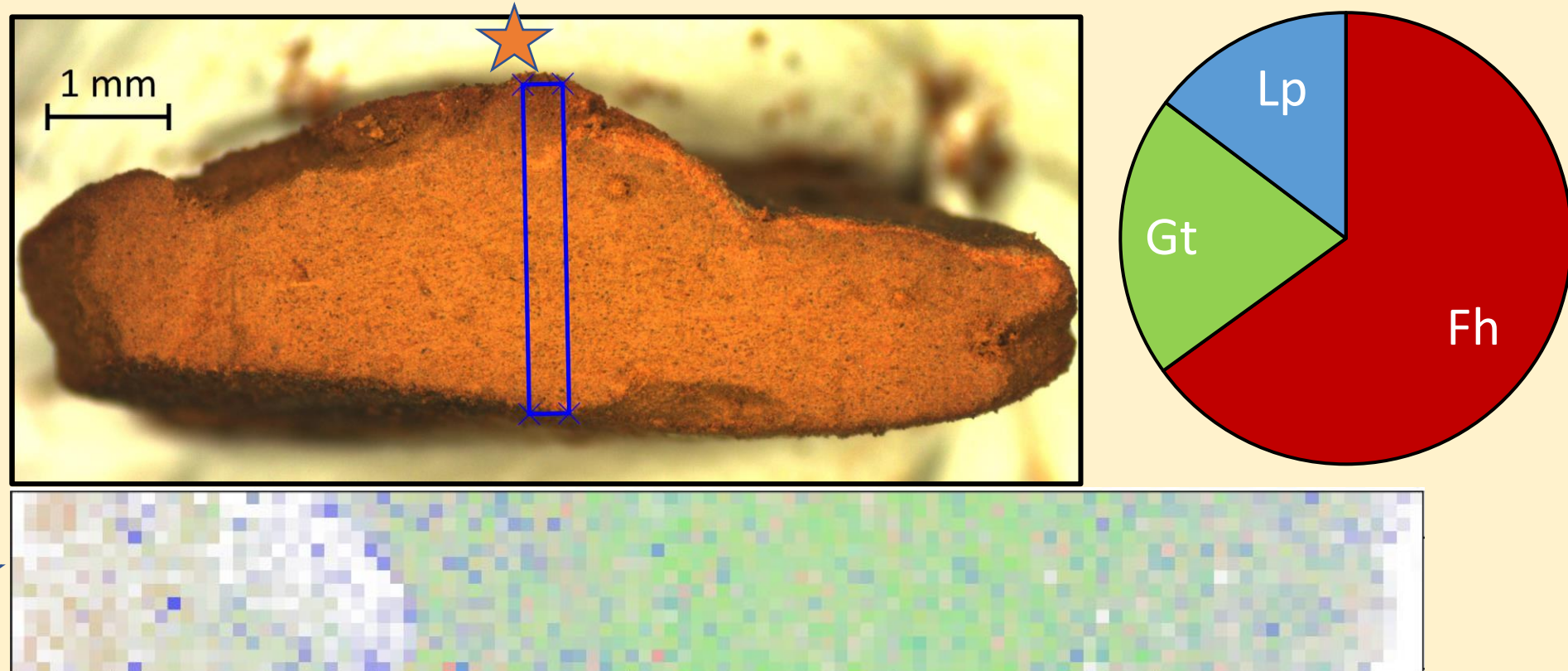


6. Crushed samples of the mineral were measured by X-Ray diffraction to determine bulk composition.

## Results

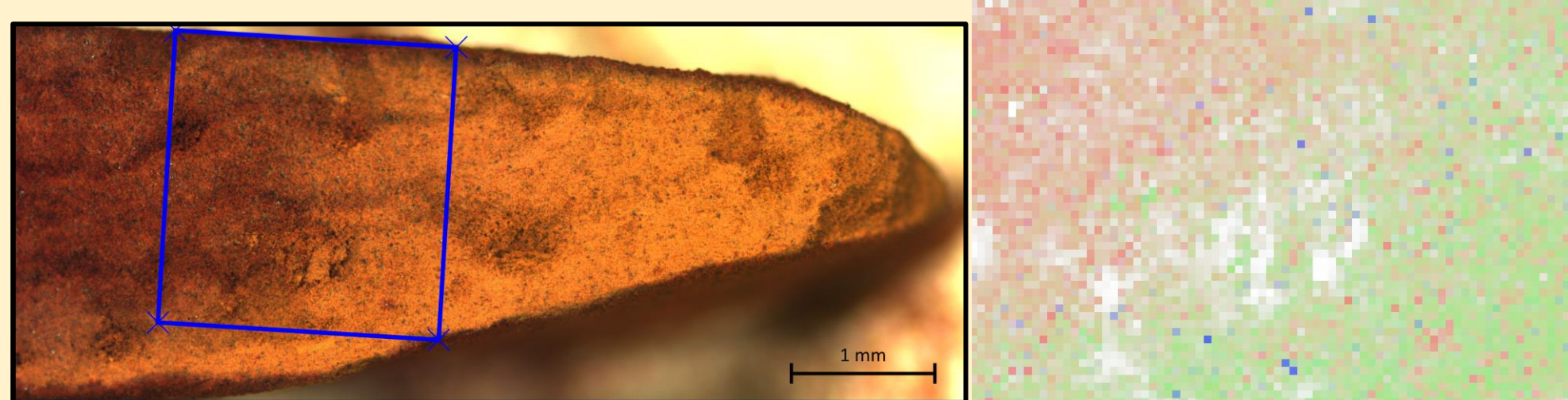
### Microcosm 1: Bangkok Plain, Thailand.

Top soil, clay, acid sulphate soil, rich in S and Fe (up to 650 and 550 mg/L pore water respectively).



### Microcosm 3: Hunan, China.

Top soil, sandy loam, moderate Fe and DOC release.

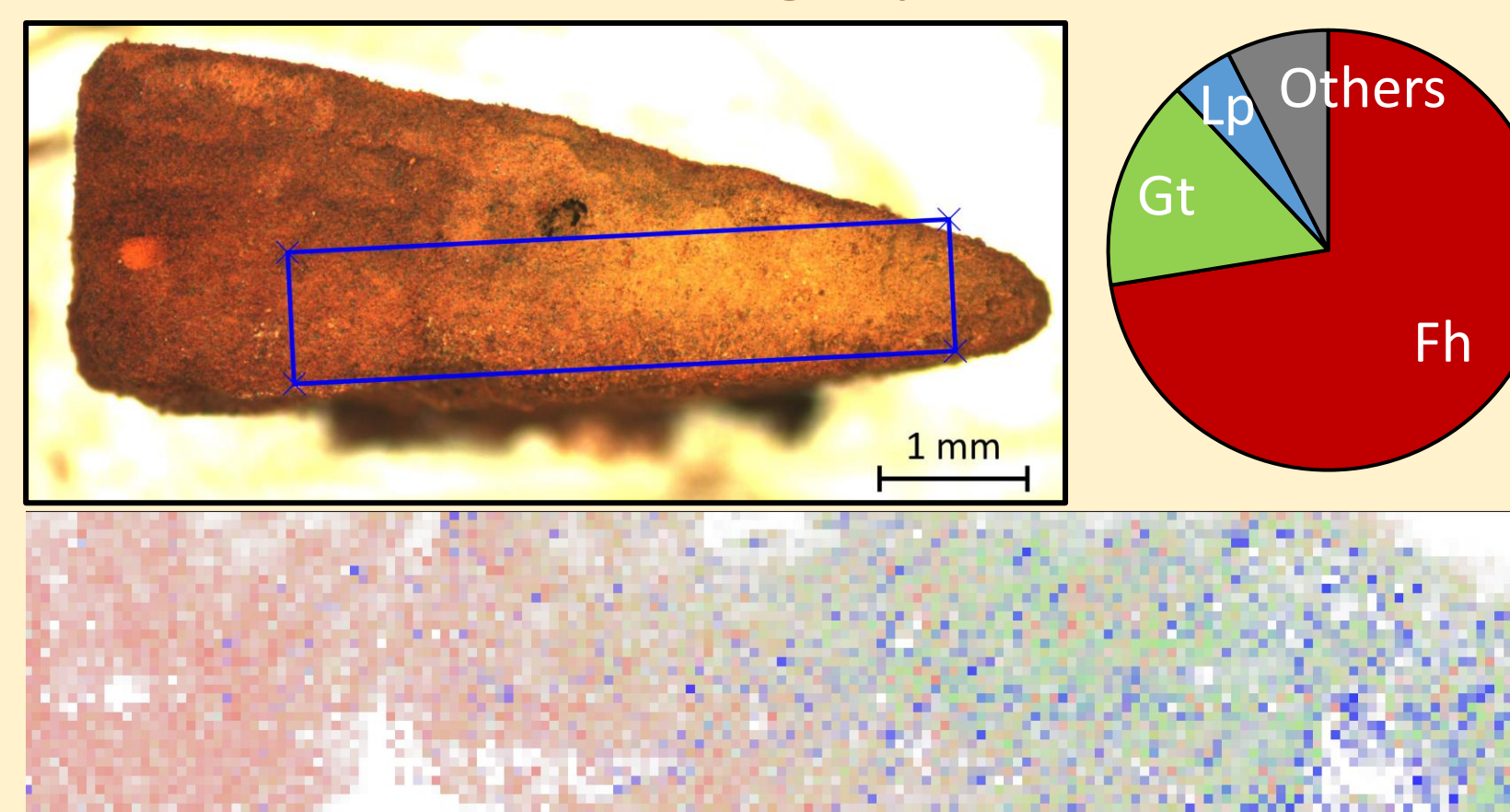


### Microcosm 5: Bangkok Plain, Thailand.

Top soil, clay, acid sulphate soil, redox inactive. No Fh transformation detected.

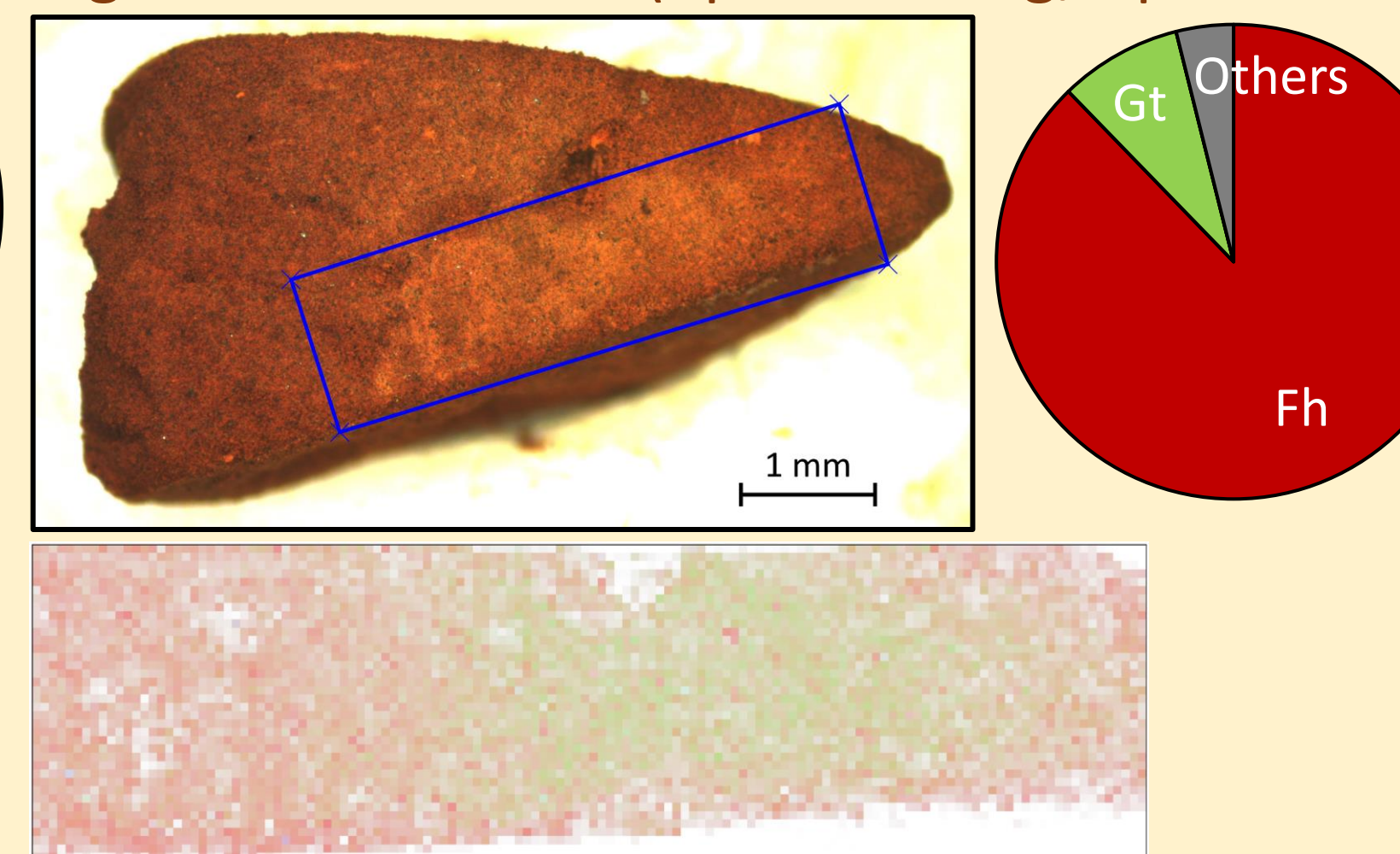
### Microcosm 2: North-East Thailand.

Top soil, sandy loam, highly weathered, rich in reducible iron (> 500 mg/L pore water).

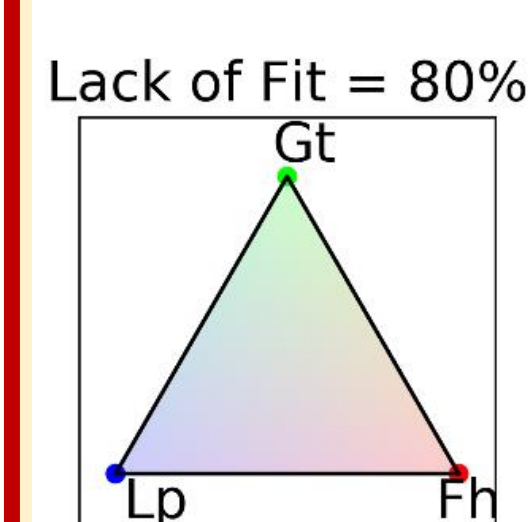
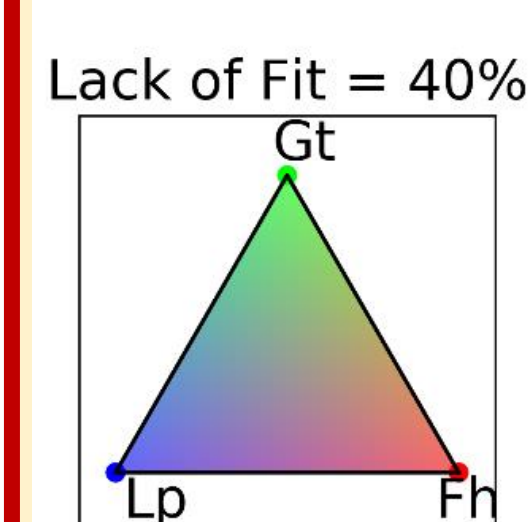
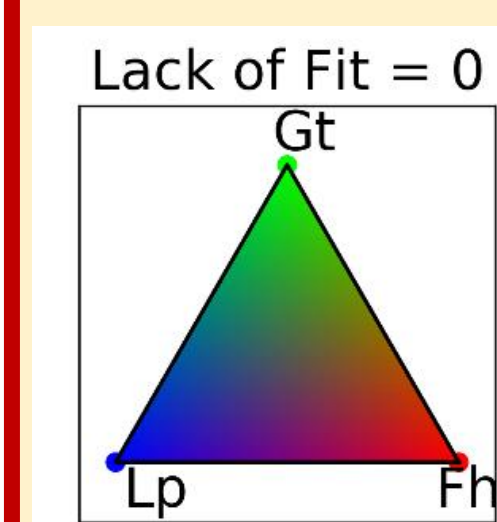


### Microcosm 4: Dhaka region, Bangladesh.

Top soil, loam, Holocene (young) sediment, highest DOC release (up to 400 mg/L pore water)



## How to read the figures



- Ferrihydrite
- Goethite
- Lepidocrocite
- Others (not iron minerals)

The cross-section surfaces are photographed with a microscope camera. The regions marked in blue indicate the area which was mapped with the Raman microscope.

The Raman spectrum maps are made up of pixels with three colour components, scaled to the abundance of Fh (red), Gt (green) and Lp (blue), according to the legend in this box. Pale colours indicate a lack of fit in the component analysis.

The pie charts indicate the abundance of iron minerals in the bulk after 2 weeks, based on Reitveld analysis of XRD spectra.

## Conclusions

- **Goethite is the most abundant mineral following transformation.** Despite the onset of reducing conditions, and high S loads in some soils, sulphide minerals were not observed. Furthermore magnetite was not observed, as might have been expected based on the concentration of Fe alone [4].
- **Mineral transformation pathways vary in different soil environments, likely due to variation in the composition of the pore water.** The speed of transformation varied between soil microcosms, and the proximity to soil affects mineral transformation.
- **Lp may not be acting as a pre-cursor to Gt in these systems.** The abundance of Lp is largely dependant on the soil treatment, but mostly co-occurs with Gt.
- **We suggest that Fh in the interior is somewhat protected from reductants in the pore water, while components of pore water that stabilise Fh are active at the interface of the soil and mineral.** However, each soil has a unique distribution, and the effect of Fh stabilisation is more or less visible after incubation in certain soils.



- [1] Borch, T., Kretzschmar, R., Kappler, A., van Cappellen, P., Ginder-Vogel, M., Voegelin, A. & Campbell, K. 2010: Environ. Sci. Technol., 44, 15-23.  
[2] Dittmar, J., Voegelin, A., Maurer, F., Roberts, L. C., Hug, S. J., Saha, G. C., Ali, M. A., Borhan, A., Badruzzaman, M. and Kretzschmar, R. 2010: Environ. Sci. Technol., 44: 8842-48.  
[3] Hansel, C. M., Benner, S. G. & Fendorf, S. 2005: Environ. Sci. Technol., 39, 7147-7153.  
[4] Hansel, C. M., Lentini, C. J., Tang, Y., Johnston, D. T., Wankel, S. D. & Jardine, P. M. 2015: ISME J., 9, 2400-2412  
[5] Tronc, E., Belleville, P. & Jolivet, J.-P. 1992: Langmuir, 8, 313-319.

We gratefully acknowledge the assistance of Kurt Barmettler (ETH Zurich Soil Chemistry Laboratory technician) and Worachart Wisawapipat (Kasetsart University, Thailand) and Xu Fang (ETH Zurich Soil Chemistry). This research is part of a project that has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme ((788009-IRMIDYN-ERC-2017-ADG).

ETH zürich

