

Formation of metal & OM-rich microaggregates in meso-density fractions
(1.8-2.4 g cm⁻³) assisted by “organo-metallic glue”

Implications for “soil C saturation” (clay only?) and “aggregate hierarchy”

Co-localization of iron and aluminum with organic matter across a range of soils: a density-based approach

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Background & Question

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Experimental studies revealed mechanisms of OM-metal interactions (adsorption, complexation, and co-precipitation). **But we know little on which mechanisms work at where within bulk soils**

Extractable Fe & Al correlate well with SOM in many soils (but, not in all soils)

- TOC: Tiessen et al. 1984; Skjemstad et al. 1989; Wada, 1995; Kasier & Guggenberger 2000, Percival et al. 2000
- ^{14}C : Torn et al., 1997; Masiello et al., 2004
- Global significance: Rasmussen et al. 2018; Kramer & Chadwick, 2018; La Londe et al. 2012

→ **Potentially useful for SOM modeling**

What do these metal phases represent?

- Pyrophosphate (PP)
- Acid Oxalate in Dark (OX)
- Dithionite Citrate (DC or DCB)



→ **Metal extraction techniques: not so selective**

(Parfitt and Childs, 1988; Rennert, 2019)

→ **Important to clarify the nature of the Fe/Al phases & their role in OM stabilization**

Metal phase	pH			
	6-8 DC	7-8 AC	3 OX	10 PP
Monomer (Fe-OM complex)	⊙	⊙	⊙	⊙
<u>Ferrihydrite</u>	⊙	⊙	⊙	<i>d</i>
<u>Lepidocrocite</u> /Magnetite	○	○	△	×
Goethite	⊙	×	×	<i>d</i>
Hematite	○	×	×	<i>d</i>
Monomer (Al-OM complex)	⊙	⊙	⊙	⊙
Allophane/ <u>imogolite</u>	○	△	⊙	△
Gibbsite	×	△	△	<i>d</i>
<u>Halloysite</u>	×	×	×	×
Kaolinite	×	×	×	×

(Wagai et al. 2013, based on Parfitt & Childs, 1988 and Reyes & Torrent, 1997)

Question 1: where do Fe/Al phases locate within bulk soils?

→ **which types of organo-metal interaction in what kinds of micro-environment?**

Question 2: any general relationship across a wide range of soils?

Method: sequential density fractionation X sequential metal extraction (PP, OX, DC)

Methods & Results

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23 soil samples of contrasting mineralogy

- A horizons + 2 spodic horizons + 3 buried A horizons
- 5 soil orders
 - Andisols, Spodosols, Inceptisols, Mollisols, Ultisols
- 5 climate zones
- 3 land use (Cropland, Grassland, & Forest)

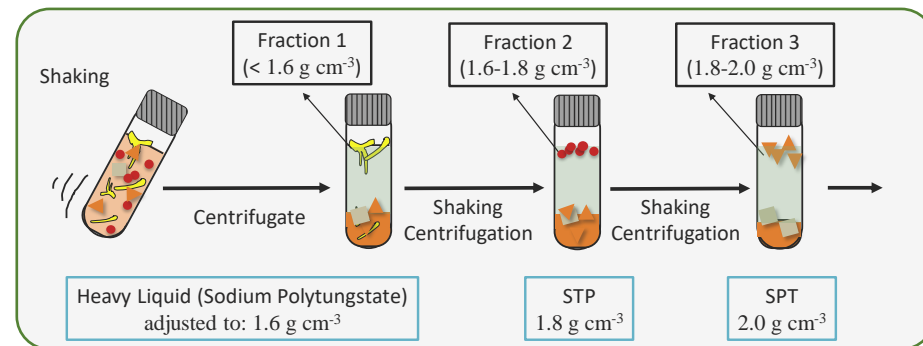


Sequential density separation

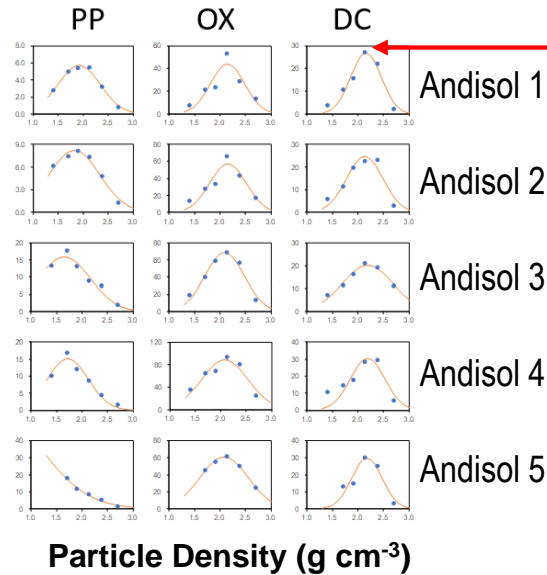
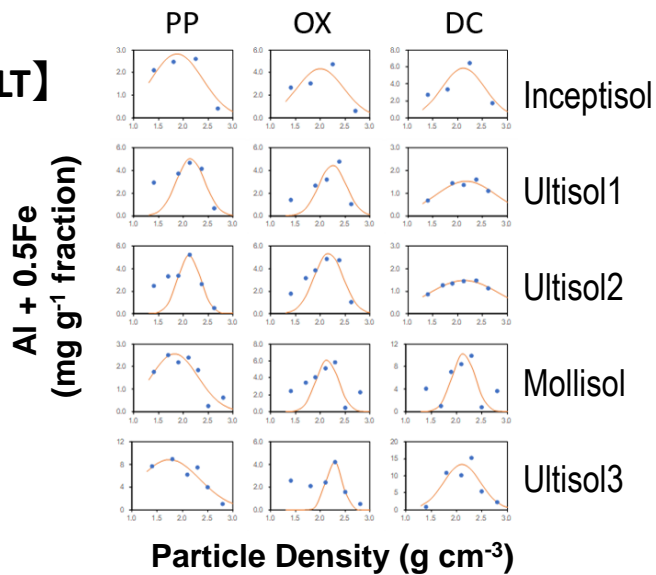
- into 4 to 7 fractions
- Dispersion by mechanical shaking

Each density fraction extracted by

- PP → OX → DC reagents



【RESULT】



Peak density identified for each soil & each metal phase

Metal enrichment in meso-density (1.8-2.4 g cm⁻³) across 23 soils

Major findings

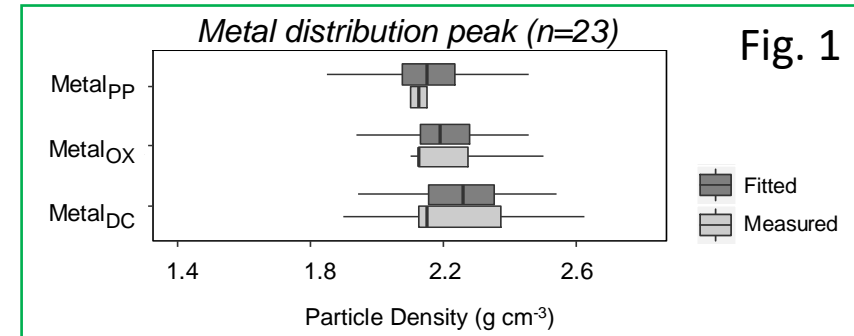
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● Metal concentration

- All extractable Fe & Al phases peaked at 1.8-2.4 g cm⁻³ across the 23 soil samples
- Peak density of PP-extr. Fe&Al was lower by 0.3-0.4 g cm⁻³ rel. to OX- and DC-extr. phases

● Metal distribution (mass distribution x metal conc.)

- All metal phases were localized in narrower meso-density range (ca. 2.1 g cm⁻³), Fig. 1
- C & other minerals were mainly present in meso-density (Fig. 2) → **Microaggregate formation (Fig. 3)**

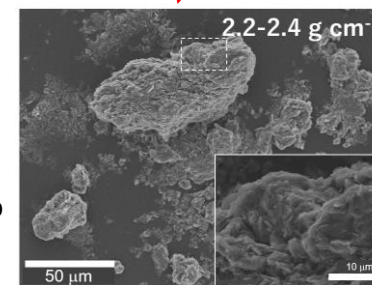
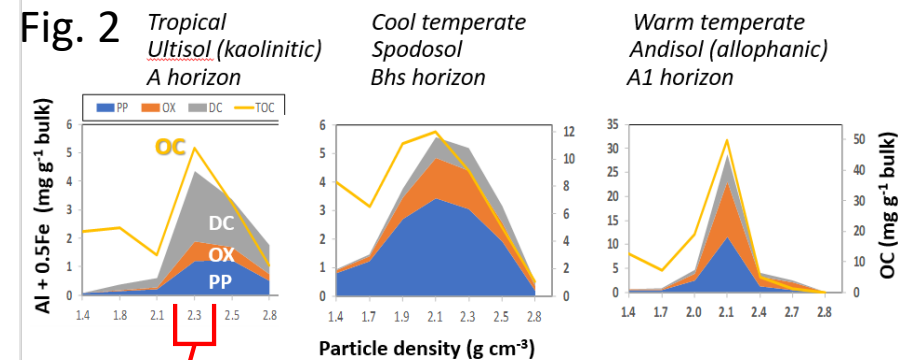


● OM characteristics

- Meso/high density = lower C:N, ¹³C, ¹⁵N enriched
- Significant positive correlation between metal and co-dissolved C in PP (& OX) extracts across soils and among density fractions w/i soil

● Why constant OC:metal in PP (& OX) extracts?

- Simplest explanation: “organo-metallic unit” (PP-extractable phase) act as “glue”
- **“Organo-metallic glue” hypothesis** helps to link nanoscale interaction (e.g., Tamrat et al. 2019) with microaggregate formation (e.g., Totsche et al. 2017; Asano et al., 2018) and with physical fractionation results.



20-200 μm sized aggregate formation promoted presumably by organo-metallic glue

Fig. 3