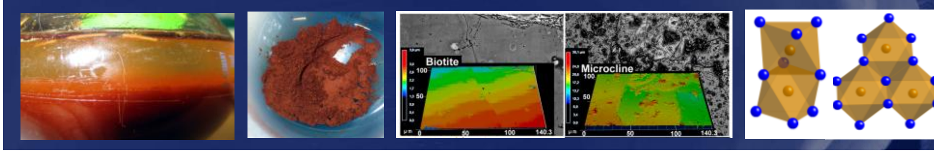
Leibniz Universität Hannover

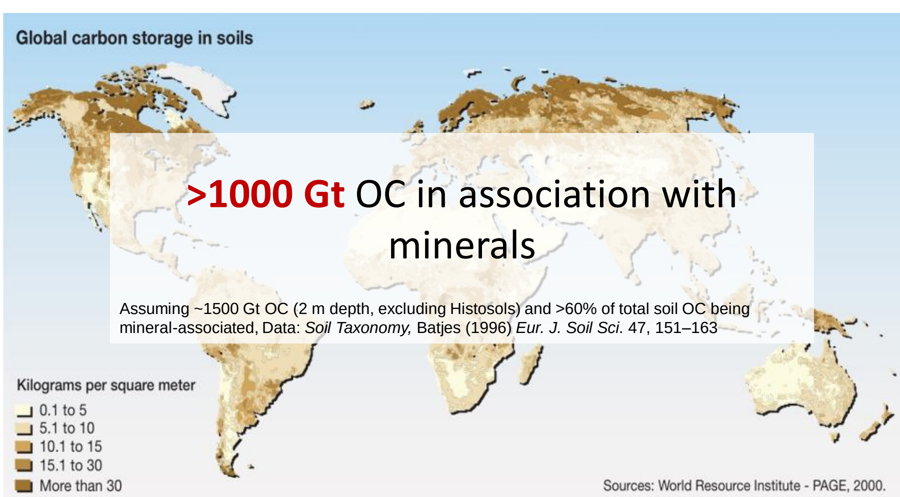
22-24.9.2014 Summer-School, Krasnojarsk



Mineral-organic Associations: Formation, properties, and functions

Robert Mikutta, Institute of Soil Science, Hannover, Germany

Introduction | Krasnojarsk, 2014



>1000 Gt OC in association with minerals

Assuming ~1500 Gt OC (2 m depth, excluding Histosols) and >60% of total soil OC being mineral-associated, Data: *Soil Taxonomy,* Batjes (1996) *Eur. J. Soil Sci.* 47, 151–163

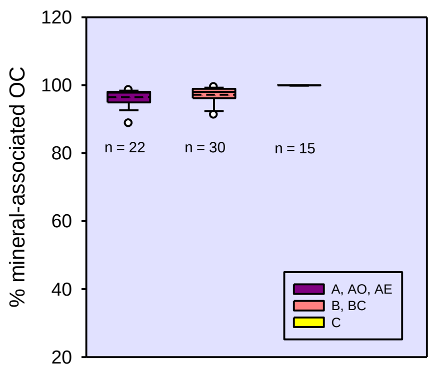
Global importance

Introduction

Krasnojarsk, 2014

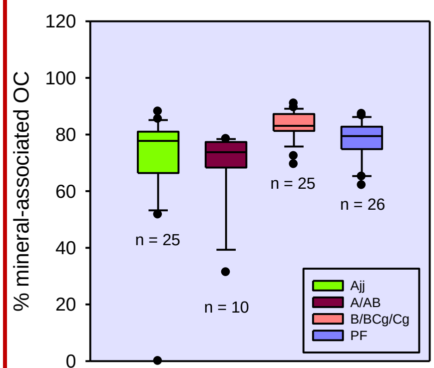
Under extreme conditions

wet (MAP 3000-6000 mm)



New Zealand, 120 Kyr chronosequence

cold (MAT -12°C)

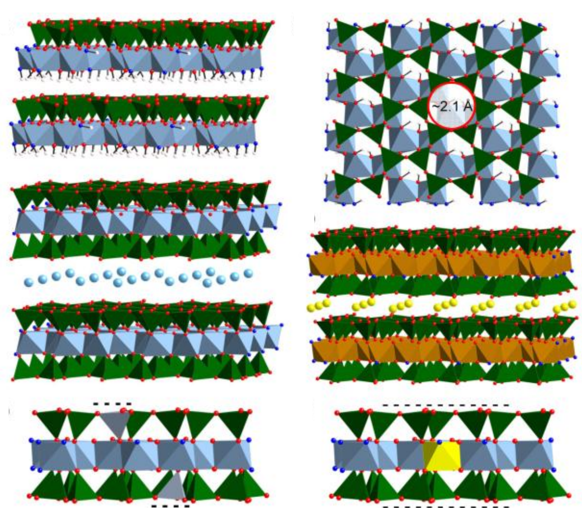


Siberian tundra soils

Global importance

Introduction

Krasnojarsk, 2014



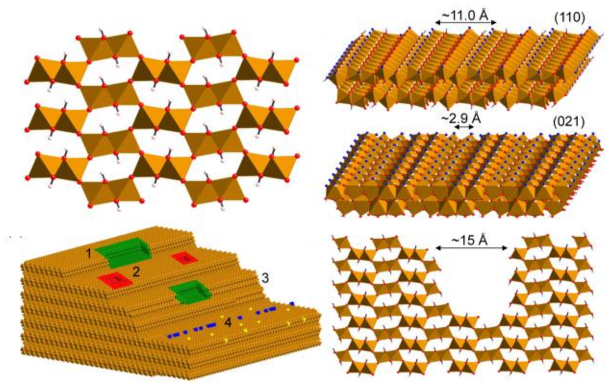
Clay minerals

SSA
10-800 $m^2\ g^{-1}$

PZC
<5

The reaction partners

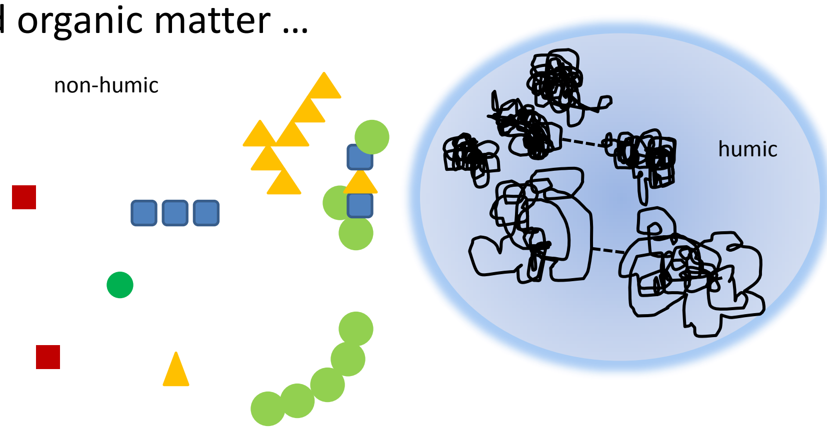
Metal (hydr)oxides

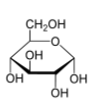


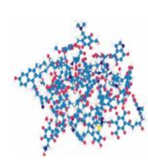
SSA
5-500 m^2 g^{-1}

PZC
7-9

and organic matter …







Size and complexity

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Concepts & Ideas

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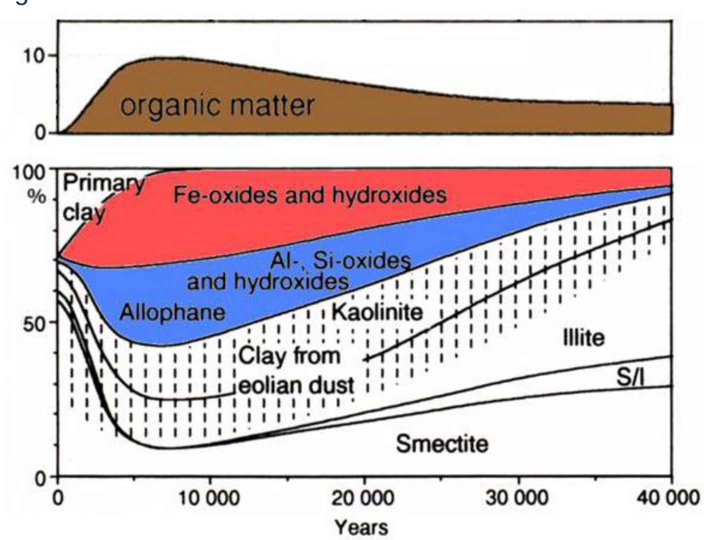
Regosols Andosols Luvisols



Jahn et al. (1992) *Miner. Petrogr. Acta* **35A**, 193–201

Mineral-transformations

Concepts & Ideas

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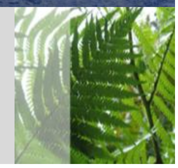
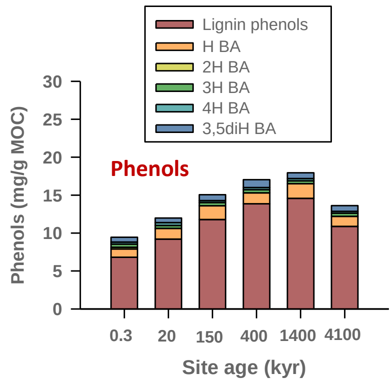
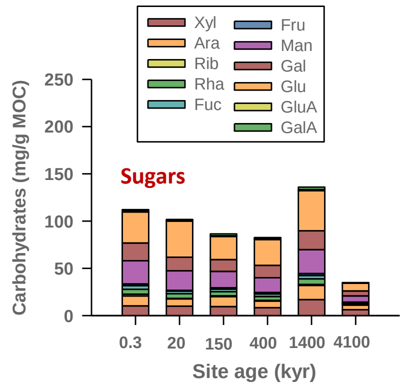
Chronosequence
at Hawaiian Islands
0.3–4,100 Kyrs







BA = benzoic acid

Mikutta R. et al. (2009) *Geochim. Cosmochim. Acta* **75**, 5122-5139

Selectivity in organic matter accumulation

Concepts & Ideas

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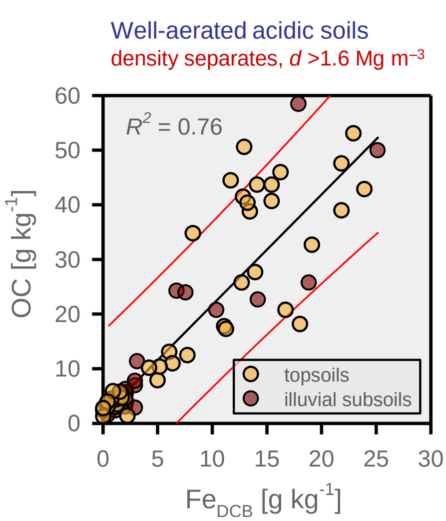
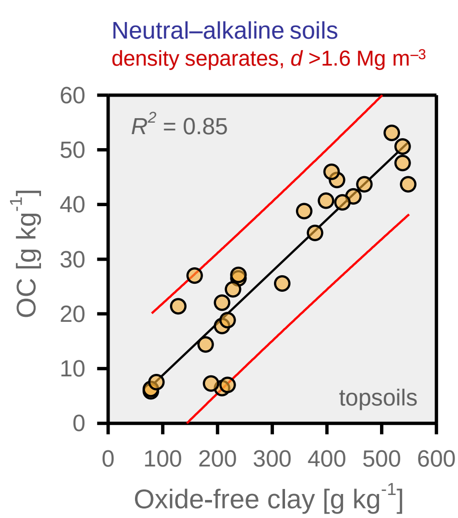
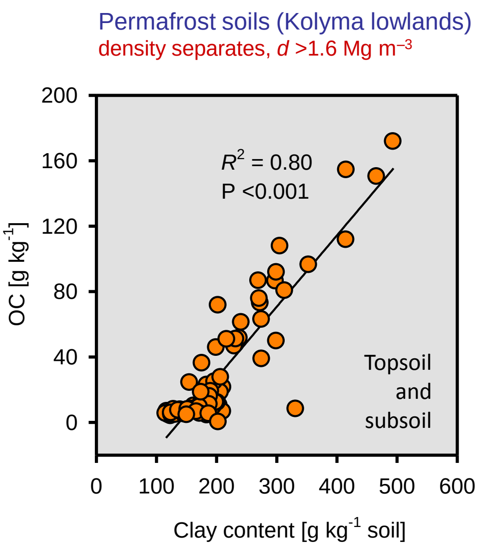




Kaiser K & Guggenberger G (2000) *Org. Geochem.* 31, 711–725

Selectivity in organic matter accumulation

Concepts & Ideas — Krasnojarsk, 2014



No correlation with total pedogenic Fe (DCB-extractable Fe) !

Reason: Reductive dissolution of Fe(III) oxides

Selectivity in organic matter accumulation

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Mineral	specific surface area	maximum C sorption	
	$m^2\ g^{-1}$	$mg\ C\ m^{-2}$	$mg\ C\ g^{-1}$
Kaolinite	11–26	0.1–0.3	1.1–7.8
Illite	24–77	0.1–0.2	2.4–14.4
Vermiculite	15–70	0.1–0.2	1.5–14.0
Smectite	14–287	0.2–0.3	2.8–86.1
Hydroxy-interlayered clays	3–80	0.1–0.4	0.3–32.0
amorphous $Al(OH)_3$	12–285	0.3–1.1	3.6–313.5
Gibbsite	19–63	0.1–0.5	1.9–31.5
Ferrihydrite	180–500	0.3–1.2	54.0–600.0
Haematite	4–87	0.2–1.1	0.8–95.7
Goethite	11–185	0.2–2.1	3.4–388.5
Allophane / Imogolite	280–580	0.5–0.9	140.0–522.0

Kaiser K & Guggenberger G (2000) *Org. Geochem.* 31, 711–725

Selectivity in organic matter accumulation

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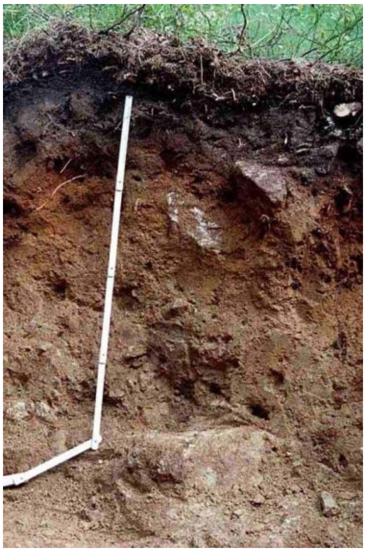
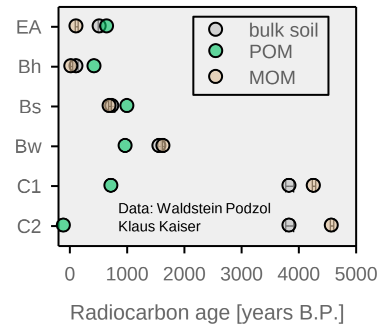




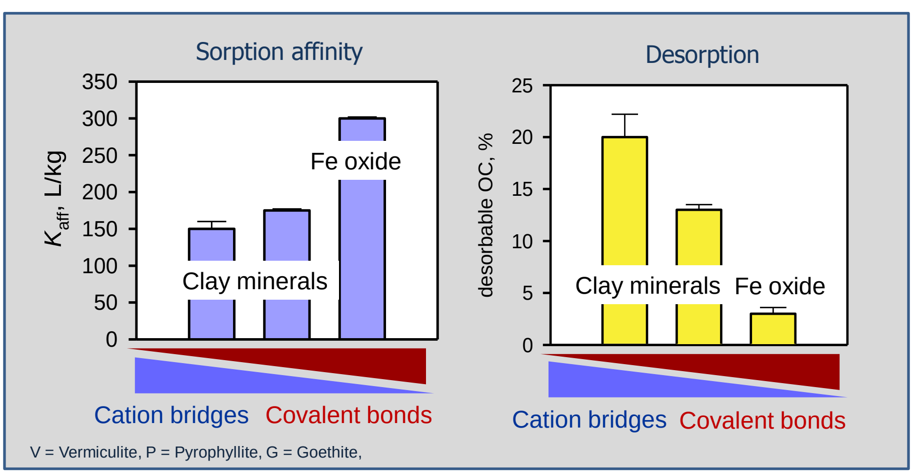
- Binding mechanisms
- Surface loading and pore clogging
- Multilayer formation

Minerals and organic matter stabilization mechanisms

Concepts & Ideas

Krasnojarsk, 2014

Organic matter adsorption to different mineral surfaces



Mineral surface reactivity and bonding mechanisms

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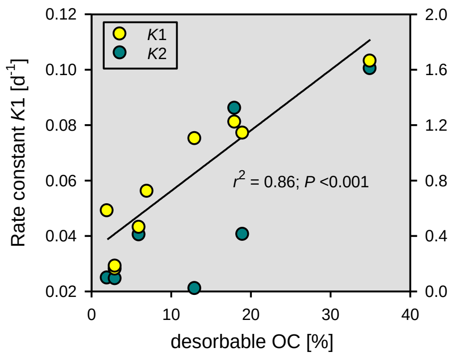
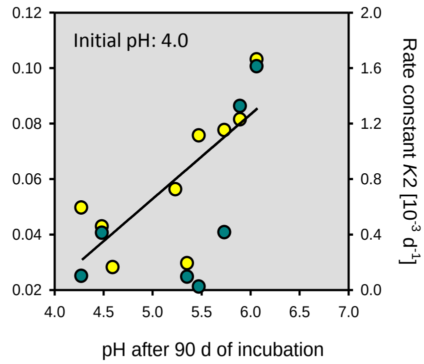
Biological stability of mineral-associated OC



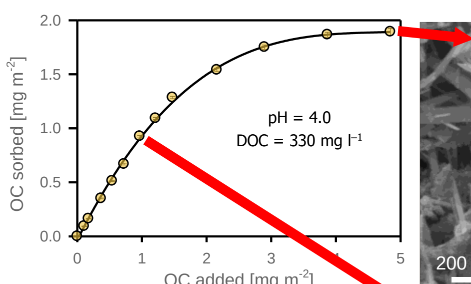


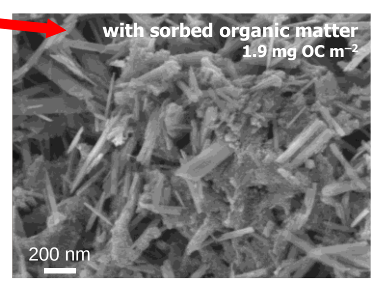
Abiotic conditions control binding strength and thus mineralization

Mikutta R. et al. (2007) *Geochim. Cosmochim. Acta* **71**, 2569–2590

Mineral surface reactivity and bonding mechanisms

Concepts & Ideas | Krasnojarsk, 2014



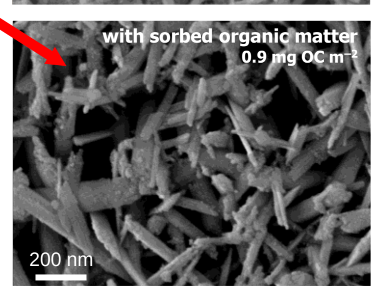


High C loading

Low biochemical stability

Low C loading

High biochemical stability

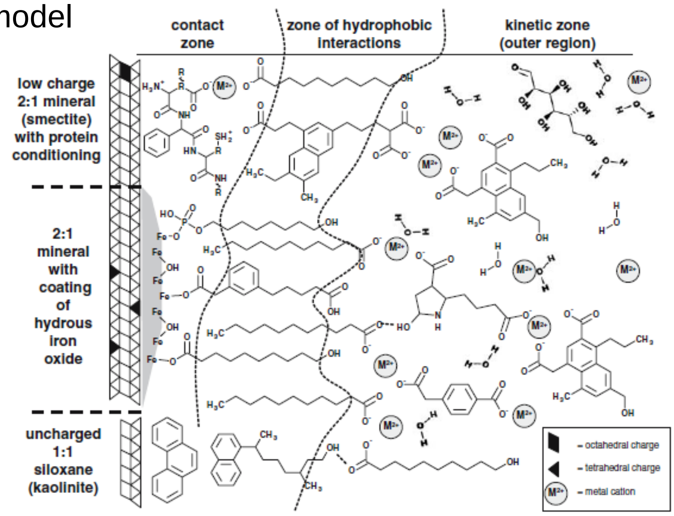


Kaiser and Guggenberger (2007) *Eur. J. Soil Science* **58**, 45–49.

Organic matter loading and octopus effect

Concepts & Ideas | Krasnojarsk, 2014

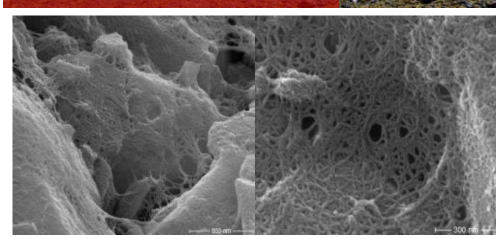
Multilayer model



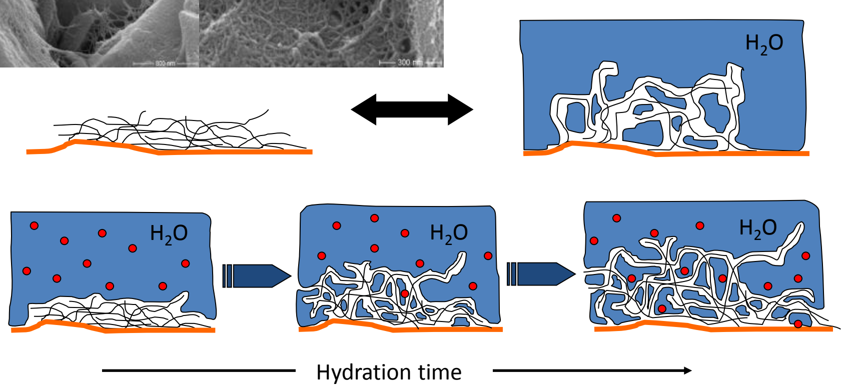
Sollins et al. (2006) *Soil Biol. Biochem.* **38**, 3313–3324
Kleber et al. (2007) *Biogeochem.* **85**, 9–24

Organization of organic coatings at mineral surfaces

Concept & Ideas | Krasnojarsk, 2014



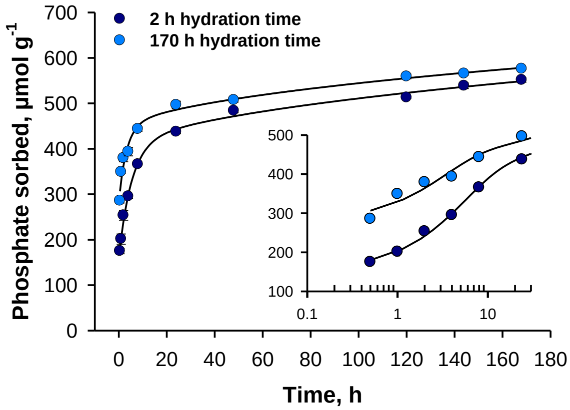
Hydration of macromolecular OM (e.g., mucilage, extracellular polymeric substances, humic compounds)



Organic matter flexibility: hydration effects

Concept & Ideas | Krasnojarsk, 2014

Phosphate sorption and organic C desorption



Phosphate faster accessible to external mineral sufaces after longer hydration time

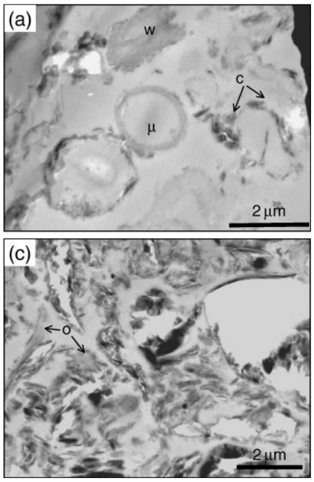
Mikutta C. et al. (2006) *Geochim. Cosmochim. Acta* **70**, 2957–2969

Organic matter flexibility: hydration effects

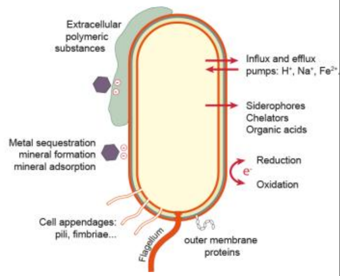
Mineral-microbe interactions | Krasnojarsk, 2014

The Bio

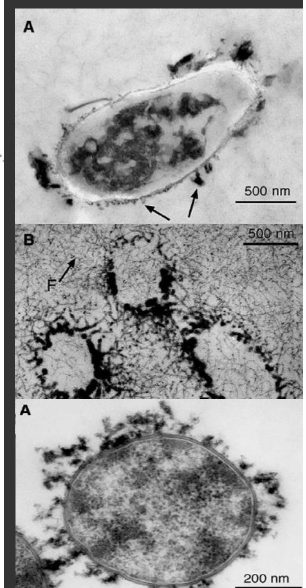
Mineral surfaces as microbial microreactors



Chenu and Plante 2006, *Eur. J. Soil Sci.*, **57**, 596–607



Handbook of Soil Science

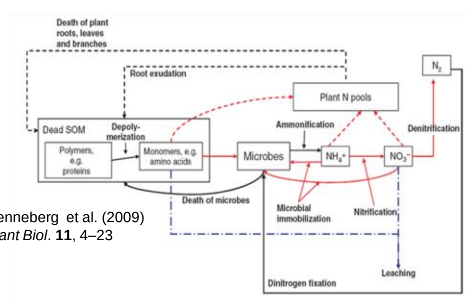


Fortin and Langley 2005, *Earth-Sci. Rev.*

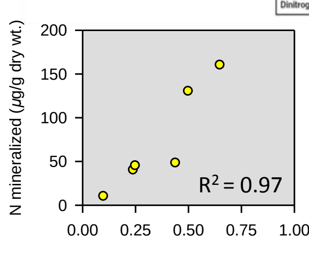
Mineral-microbe associations in soils

Mineral-microbe interactions Krasnojarsk, 2014

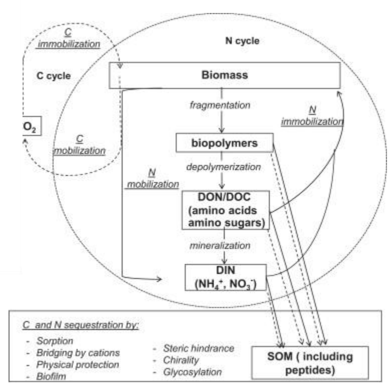
Mineral effects on C and P cycles well recognized … but



Renneberg et al. (2009) *Plant Biol.* **11**, 4–23



Re-drawn from Sollins et al. (1984) *Soil Biol. Biochem.* **16**, 31-37



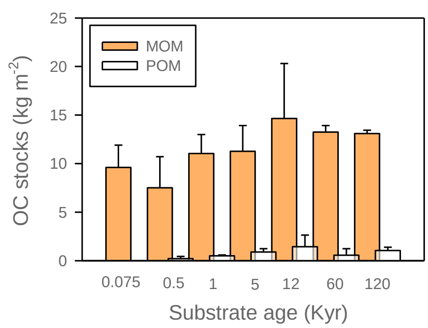
Knicker (2011) *Soil Biol. Biochem.* **43**, 1118–1129

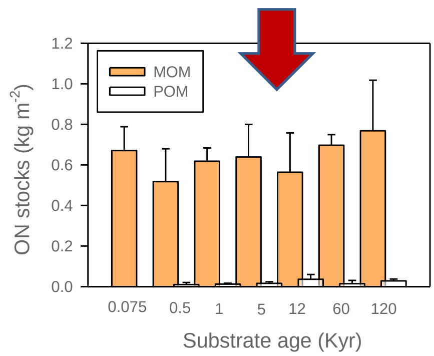
Mineral-bound OM as substrate for microorganisms

Concepts & Ideas

Krasnojarsk, 2014

Chronosequence at Franz Josef Glacier (NZ) 0.075–120 Kyrs

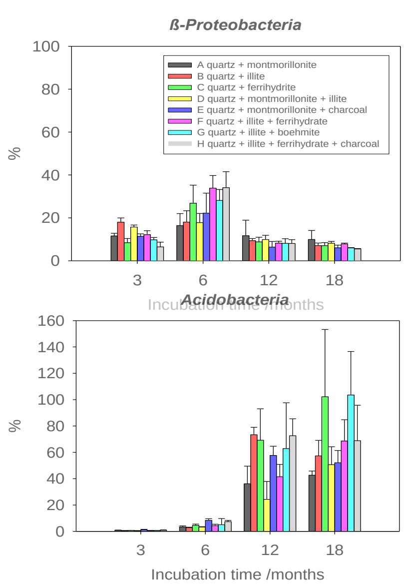




Mineral-bound OM as substrate for microorganisms

Mineral-microbe interactions

Krasnojarsk, 2014



Mineral surfaces cause modification of microbial community structure

- Artificial soils with added sterile manure
- Selective colonization of mineral surfaces by *r*- (ß-proteobacteria) and *K*-strategiest (acidobacteria)

r type: rapid growth under conditions of high resource availability

K type: lower growth rates, but higher substrate affinity

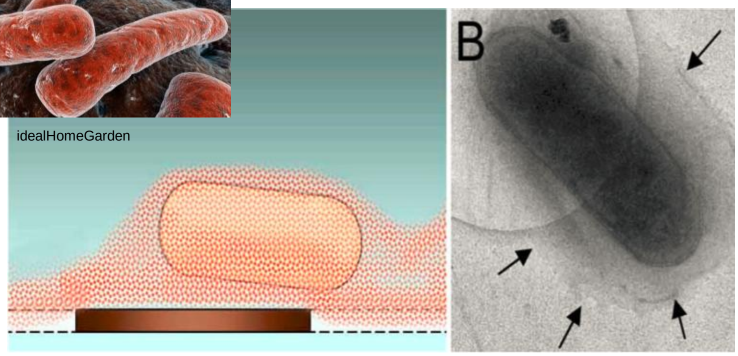
Kandeler et al. (in prep.)

Mineral surfaces as drivers for microbial community separation

Extracellular polymeric substances (EPS)

idealHomeGarden

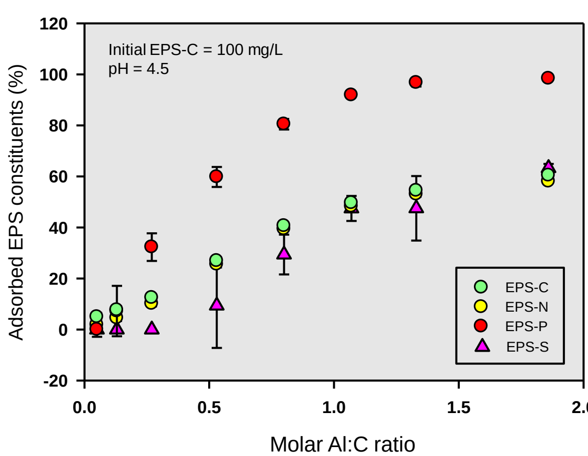
Contribution to mineral-associated OM ?



Dohnalkova et al., 2011

Mineral-microbe interactions Krasnojarsk, 2014

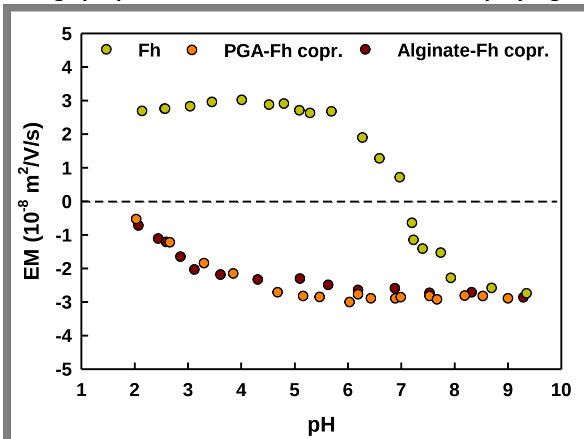
Extracellular polymeric substances (EPS) from *Bacillus subtilis* adsorbed to Al hydroxide



Mikutta, R. et al. (2011) *Geochim. Cosmochim. Acta* ***75***, 3135-3154

Microbial-derived organic matter

Charge properties of Fh and its association with polysugars



PZC

Pure Fh
7.2

PGA-Fh
~2

Alginate-Fh
~2

- Coprecipitates are net negatively charged
- Stability of suspensions at pH 7: **Fh = low, coprecipitates = high**

Mikutta, C. et al. (2008) *Geochim. Cosmochim. Acta* ***72***, 1111-1127

Charge effects of microbial compounds

Formation of mineral-organic associations:

Coprecipitation

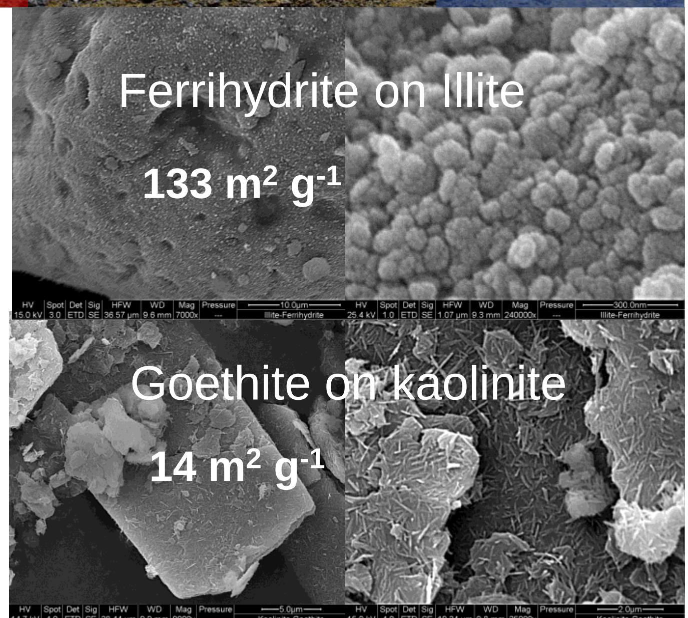
Structure & Reactivity | Krasnojarsk, 2014

Illite

115 m² g⁻¹

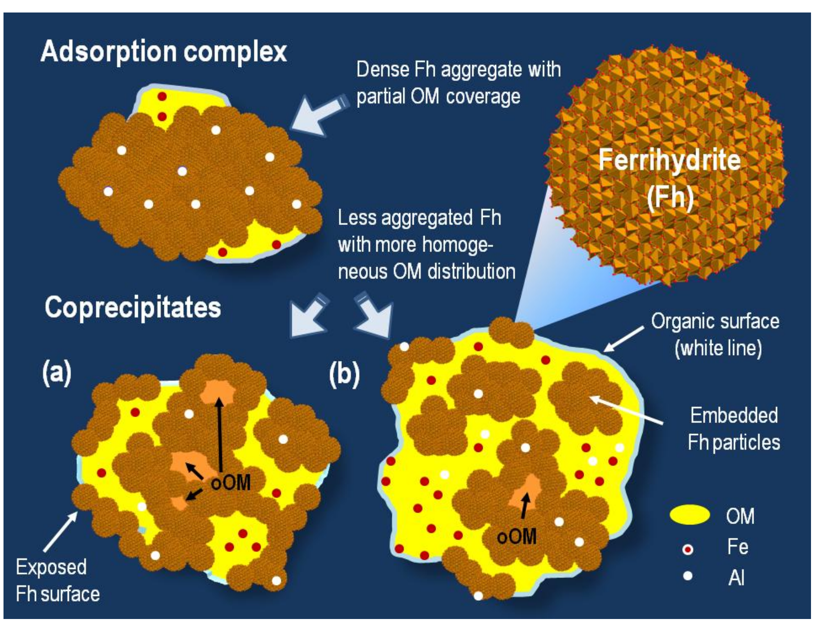
Kaolinite

7 m² g⁻¹

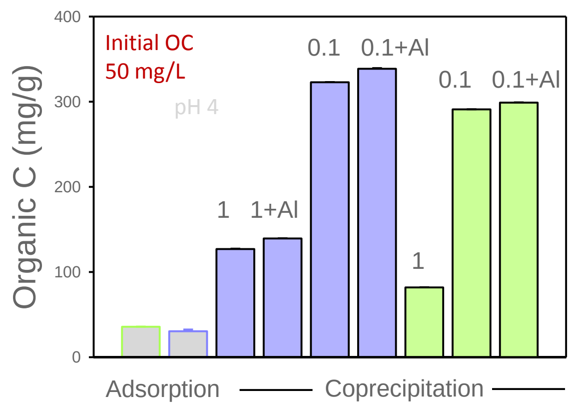


Secondary oxide precipitation modify surface properties

Introduction | Krasnojarsk, 2014



Structure & Reactivity | Krasnojarsk, 2014



Blue: Aromatic Oa
Green: Sugar-rich Oi

Adsorption versus coprecipitation

Structure & Reactivity | Krasnojarsk, 2014

Field evidence: Sediments

LETTER

doi:10.1038/nature10855

Preservation of organic matter in sediments promoted by iron

Karine Lalonde[1], Alfonso Mucci[2], Alexandre Ouellet[1] & Yves Gélinas[1]

The biogeochemical cycles of iron and organic carbon are interlinked. In oceanic waters, organic ligands have been control the concentration of dissolved iron[1]. In soils, phases shelter and preserve organic carbon[2], but the in the preservation of organic matter in sediments clearly established. Here we use an iron reductio ously applied to soils[3] to determine the amount associated with reactive iron phases in sed mineralogies collected from a wide range of environ-ments. Our findings suggest that 21.5 ± 8.6 carbon in sediments is directly bound to iron ph further estimate that a global mass of (19–45) × 10[15] organic carbon is preserved in surface marine sediments of its association with iron[4]. We propose that these ass between organic carbon and iron, which are formed through co-precipitation and/or direct chelation, pro preservation of organic carbon in sediments. Because iron phases are metastable over geological timescales, w that they serve as an efficient 'rusty sink' for organic acting as a key factor in the long-term storage of organi and thus contributing to the global cycles of carbon, oxygen and sulphur[5].

Evidence of interactions between iron and organic carbon in marine sediments was reported nearly 40 yr ago, where concentrations of iron and organic carbon were found to co-vary[6]. Because both iron and organic carbon are commonly associated with clay mineral surfaces, it was simply stated that "where there is more deposited fine-grained material with high surface area for adsorption, we find more organic

Arctic margin, the St Lawrence estuary and gulf, the Mexican margin

ducted at circumneutral pH using sodium bicarbonate as a buffer, thus preventing the hydrolysis of organic matter as well as its protonation and re-adsorption onto sediment particles, which occur under acidic conditions. Whereas the extraction of the same samples with artificial sea water released a negligible fraction of the total organic carbon (less than 3%; results not shown), samples treated under the same experi-mental conditions after substituting trisodium citrate (complexing agent) and sodium dithionite (reducing agent) for sodium chloride

> We propose that these associations between organic carbon and iron, which are formed primarily through co-precipitation and/or direct chelation, promote the preservation of organic carbon in sediments.

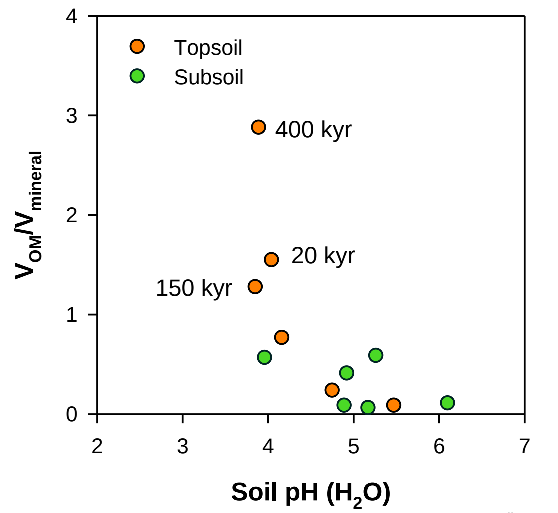
> Our data also show that the traditional sorptive stabilization mechanism, which proposes that clay particles have a preservative effect on organic matter through direct adsorption on their surfaces[4,27,28], does not describe accurately the mode of stabilization for all organic compounds in sediments.

Lalonde *et al*. (2012) *Nature* **483**, 198-200

Coprecipitation / adsorption and organic matter stabilization

Structure & Reactivity | Krasnojarsk, 2014

Field evidence: **Hawaiian Islands**

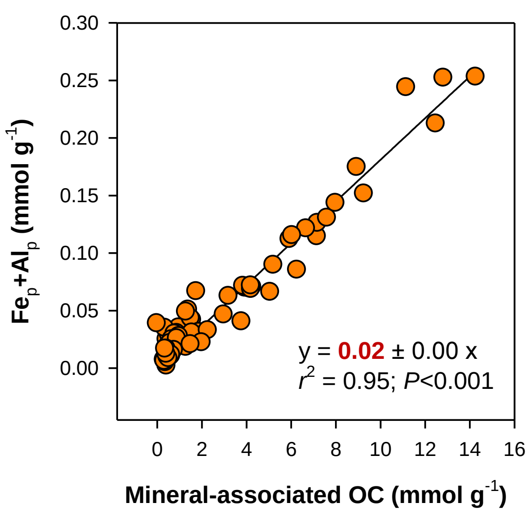


Mikutta R. et al. (2009) *Geochim. Cosmochim. Acta* **75**, 5122-5139

Adsorption versus coprecipitation

Structure & Reactivity | Krasnojarsk, 2014

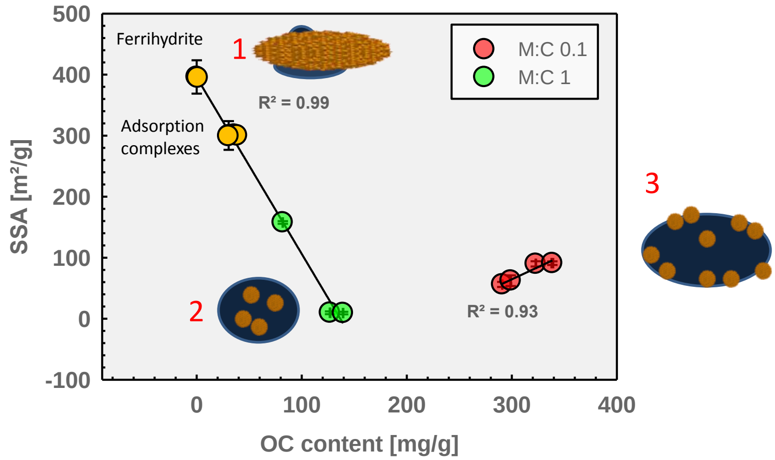
Field evidence: **Permafrost soils**



Mikutta R. et al. (2014) *Eur. J. Soil Sci.* (submitted)

Adsorption versus coprecipitation

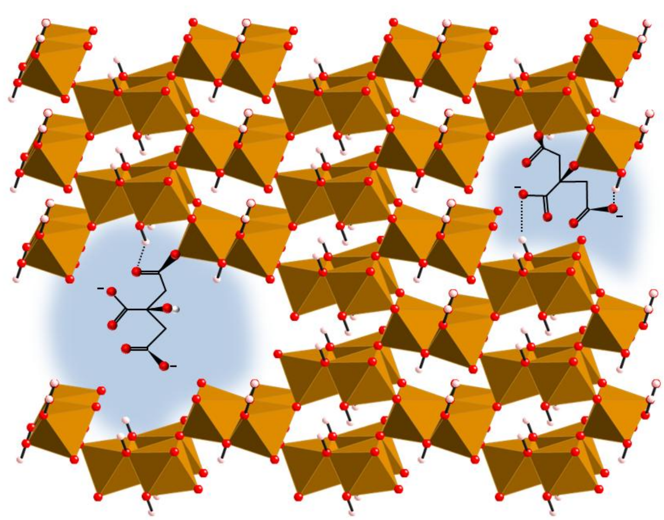
Surface properties at varying metal:C ratios



Organic matter shapes mineral phases

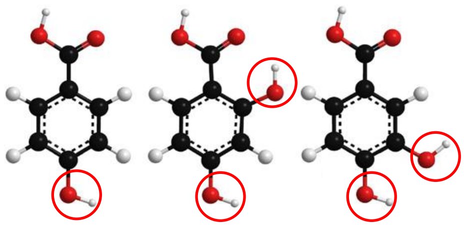
Structure & Reactivity Krasnojarsk, 2014

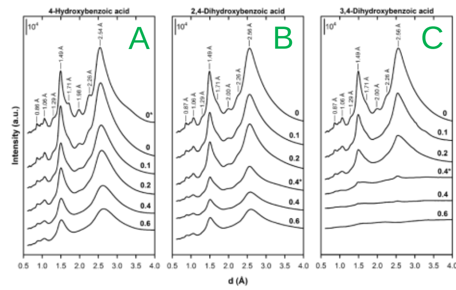
Organic matter disturbs crystallite formation



Organic matter shapes mineral phases

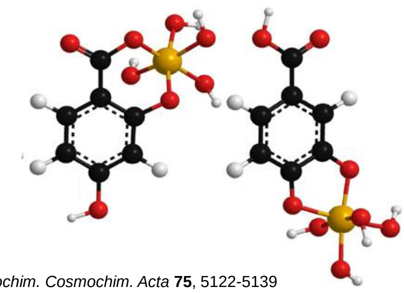
Structure & Reactivity | Krasnojarsk, 2014





Increase in Fe oxide crystallinity

→ not the total amount but **position of phenolic groups** influence HFO crystallization



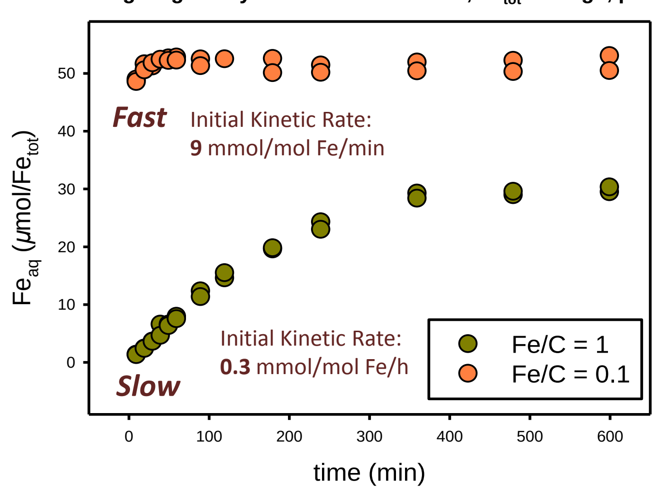
Mikutta C. (2011) *Geochim. Cosmochim. Acta* **75**, 5122-5139

Organic matter shapes mineral phases

Structure & Reactivity | Krasnojarsk, 2014

Dissolution reactions

Single ligand system: 1.5 mM oxalate, Fe_{tot} = 0.1 g/l, pH 4



Molar Fe/C ratio controls dissolution processes

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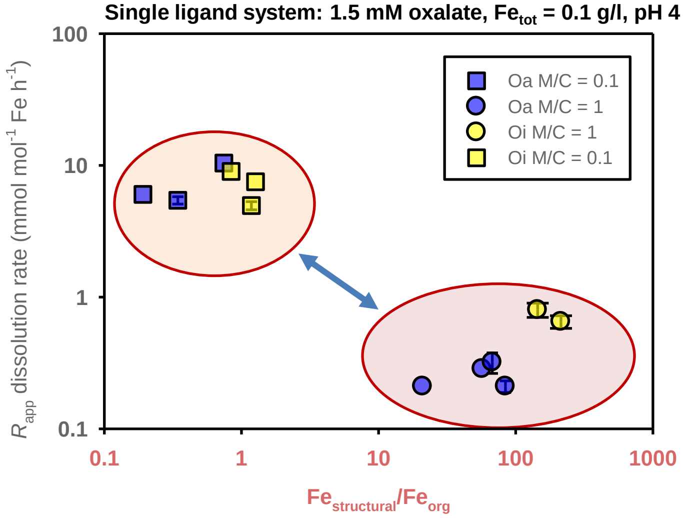
Dissolution reactions

Single ligand system: 1.5 mM oxalate, Fe_{tot} = 0.1 g/l, pH 4



Fe_{org} = pyrophosphate-extractable Fe (with ultracentrifugation 300.000 × *g* for 3 h)

Fe complexation mode controls dissolution processes

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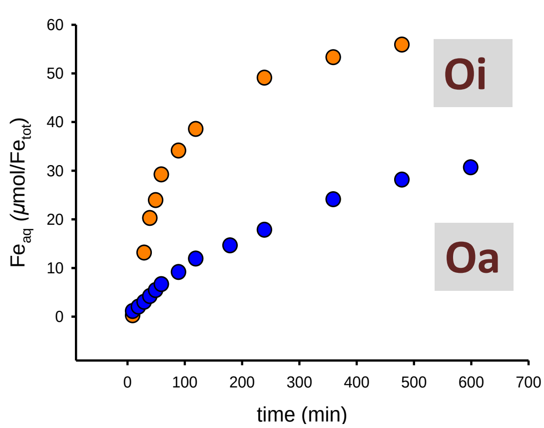
Dissolution reactions



%	Aromatic	Carbonyl /Carboxyl
Oi	**16**	**16**
Oa	**25**	**30**

Humified OM (more acidic and aromatic) binds more strongly and blocks surface sites more efficiently than litter-derived OM („Surface passivation“)

Influence of OM source on dissolution kinetics

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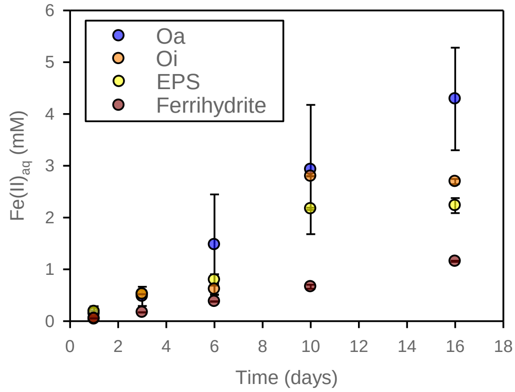
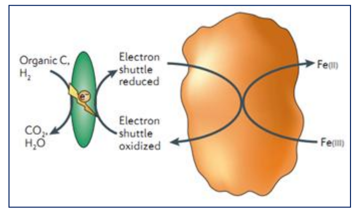
Dissolution reactions (especially relevant in permafrost soils)

Coprecipitation



Shewanella putrefaciens ➔ **Flavins**



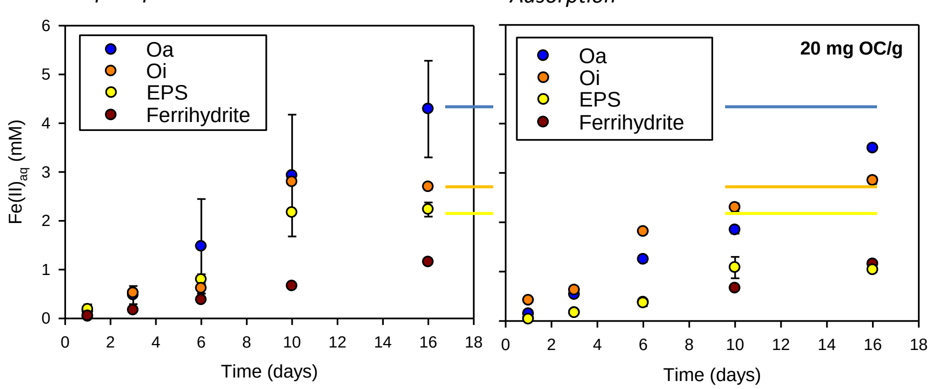
Humified OM (more acidic and aromatic) accelerates Fe reduction
➔ Electron shuttling

Influence of OM source on dissolution kinetics

Structure & Reactivity — Krasnojarsk, 2014

Dissolution reactions

Coprecipitation *Adsorption*



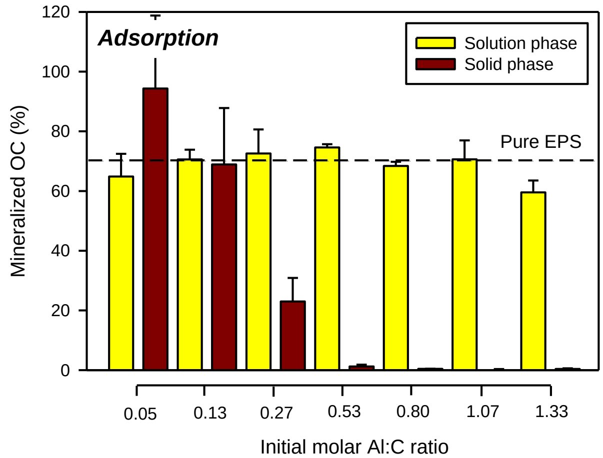
Almost similar reactivity; higher in case of coprecipitated Oa- and EPS-C

Influence of OM source on dissolution kinetics

Structure & Reactivity

Krasnojarsk, 2014

Biodegradation



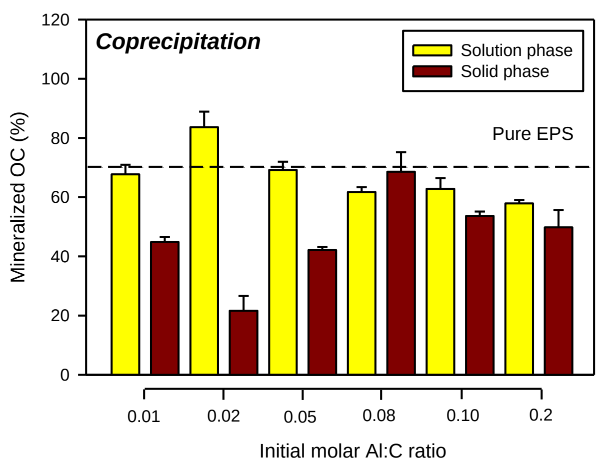
%OC	5	3	2

Coprecipitation / adsorption and organic matter stabilization

Structure & Reactivity

Krasnojarsk, 2014

Biodegradation



Mikutta, R. et al. (2011) *Geochim. Cosmochim. Acta* ***75***, 3135-3154

Coprecipitation / adsorption and organic matter stabilization

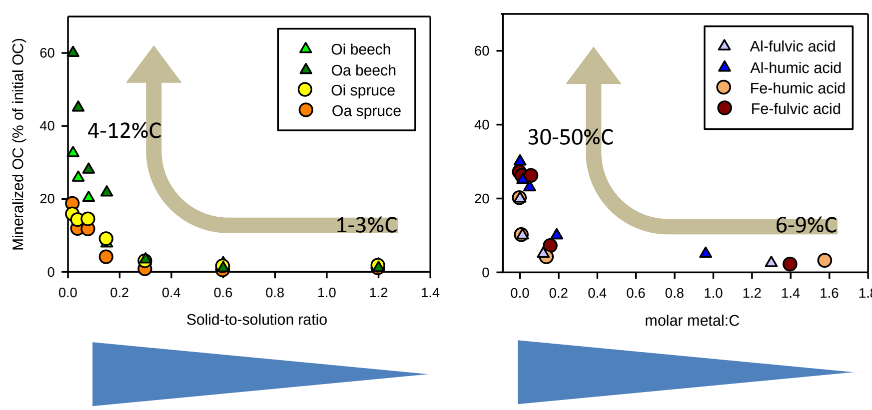
Structure & Reactivity | Krasnojarsk, 2014

DOM adsorption to Al hydroxide

(Schneider et al. 2007, *Geochim. Cosmochim. Acta*)

Artificial metal-organic complexes

(Boudot et al. 1989, *Soil Biology Biochem.*)



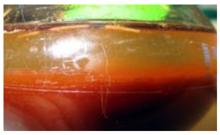
Increasing surface OC loading

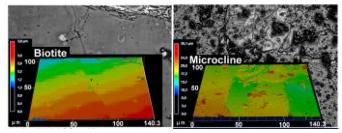
Increasing surface OC loading

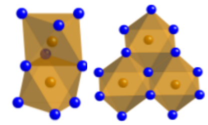
Coprecipitation / adsorption and organic matter stabilization

Take-home messages | Krasnojarsk, 2014

- Minerals control OM accumulation and stabilization in many soils
- Mineralogy changes in days to millennia and thus also the capability to accumulate OM
- Minerals accumulate OM selectively and act as nutrient sink and source (organic N and P)
- Besides adsorption, coprecipitation of OM with metals (Fe, Al, Ca) plays a role in many soil ecosystems
- Minerals reduce OM mineralization but never impair the decomposition completely
- Mineral-associated OM modifies mineral reactivity (dissolution reactions)







„Thank you“

Labour input: … many, many …

(PhD students, technicians, collaborators)

Intellectual input: … many