SUBSOIL ORGANO-MINERAL ASSOCIATIONS

UNDER CONTRASTING CLIMATE CONDITIONS

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1 Soil Science at different scales

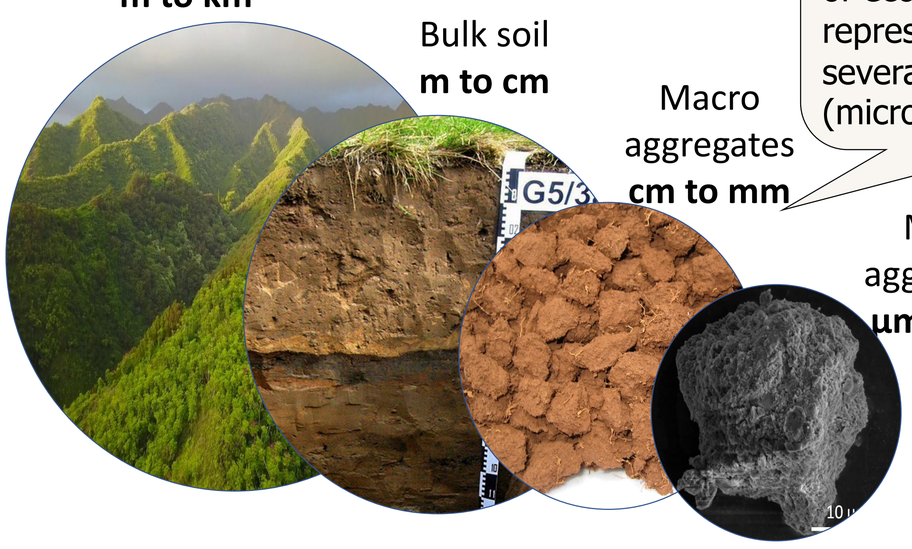
Combined approaches are crucial

Landscapes
m to km

Bulk soil
m to cm

Macro aggregates
cm to mm

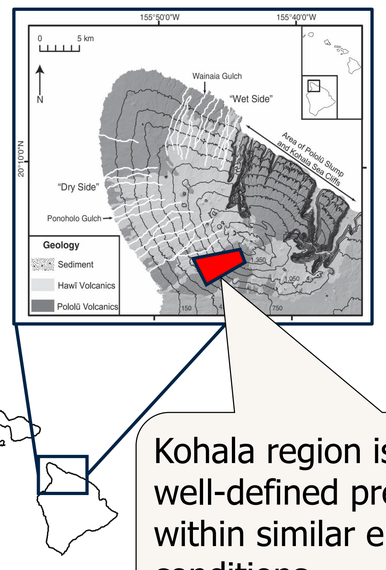
Micro aggregates
µm to nm

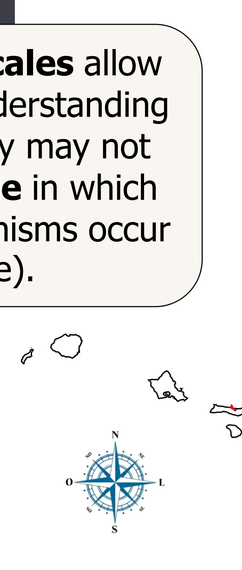


Whereas **larger scales** allow comprehensive understanding of ecosystems, they may not represent **the scale** in which several soil mechanisms occur (micro to nanoscale).

2 The experimental area

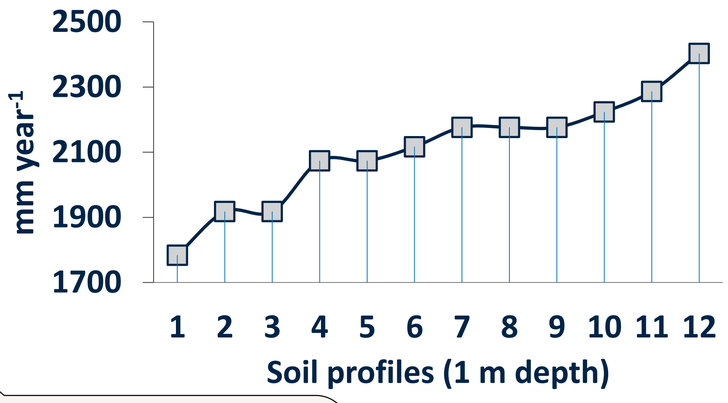
Kohala - Hawaii





Kohala region is highlighted by a well-defined precipitation gradient within similar environmental conditions

Rainfall gradient



26 Fe Iron 55.847 | 13 Al Aluminum 26.9815 | 6 C Carbon 12.011

Summary

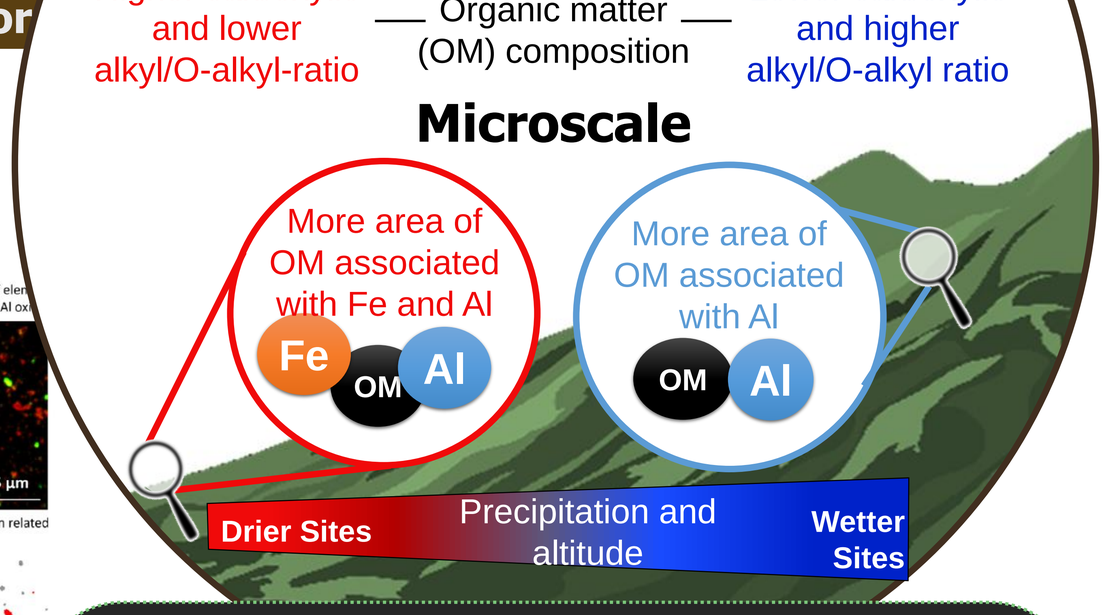
Bulk soil scale

Increase —— Fe, Al and SOC contents —— Decrease

Less reduced (Fe^{3+}) —— Fe redox state —— More reduced (Fe^{2+})

Higher carboxylic and lower alkyl/O-alkyl-ratio —— Organic matter (OM) composition —— Lower carboxylic and higher alkyl/O-alkyl ratio

Microscale

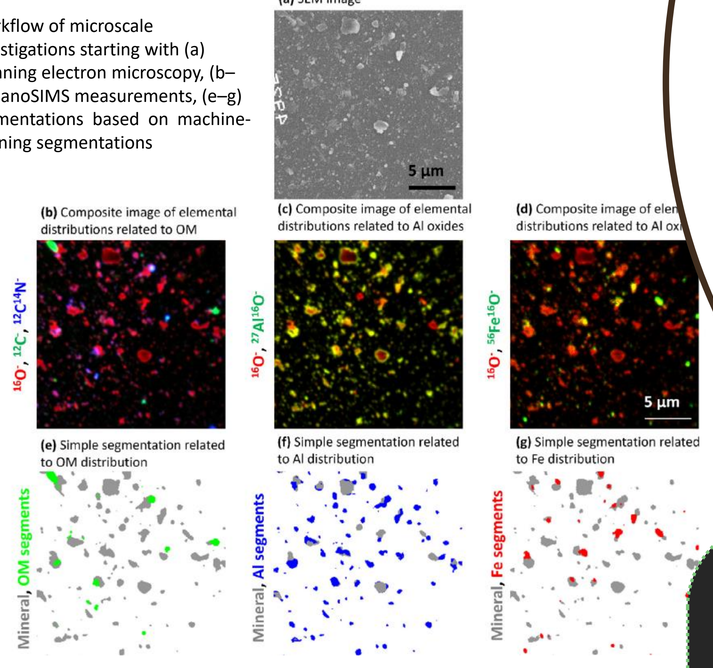


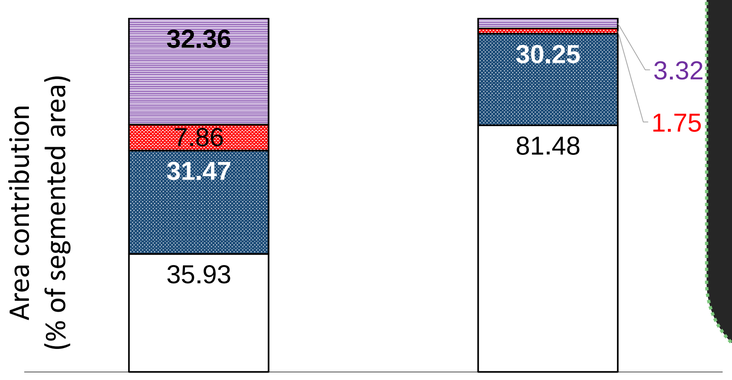
Here we demonstrate that spatial relationships between Fe and Al with SOC at the microscale display a shift towards Al-dominated SOC associations at higher precipitation that could not be ascertained from bulk measurements alone.

5 Looking at the microscale with NanoSIMS

Differences in Fe and Al behavior

Workflow of microscale investigations starting with (a) scanning electron microscopy, (b–d) NanoSIMS measurements, (e–g) segmentations based on machine-learning segmentations





Microspatial properties in <2 mm clay fraction. Area contributions of OM segment associations.

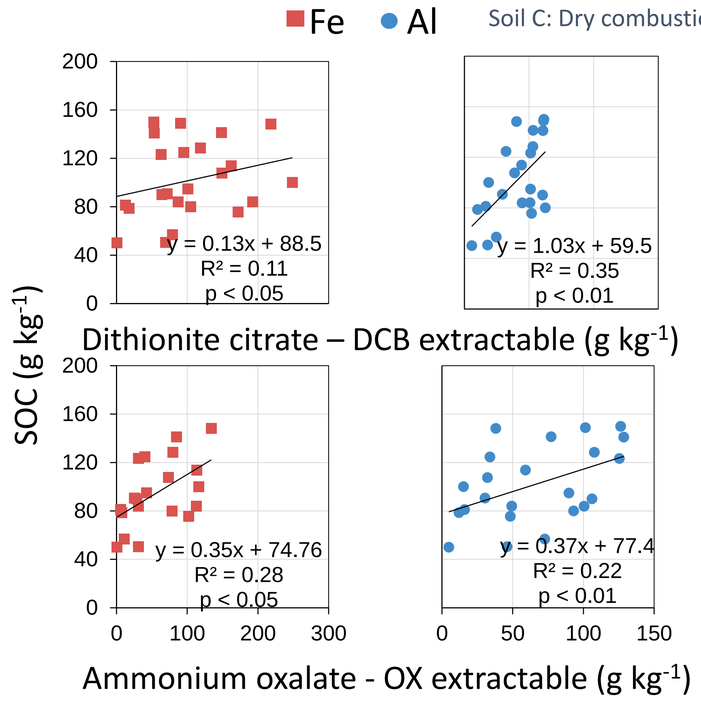
While Fe contributed to approximately 40% of the microscale organo-mineral associations in the lower precipitation site, this contribution at the higher rainfall regime was only 5%

At a higher precipitation level, OM was mostly unassociated or only associated with Al

3 Fe vs Al for SOC stabilization

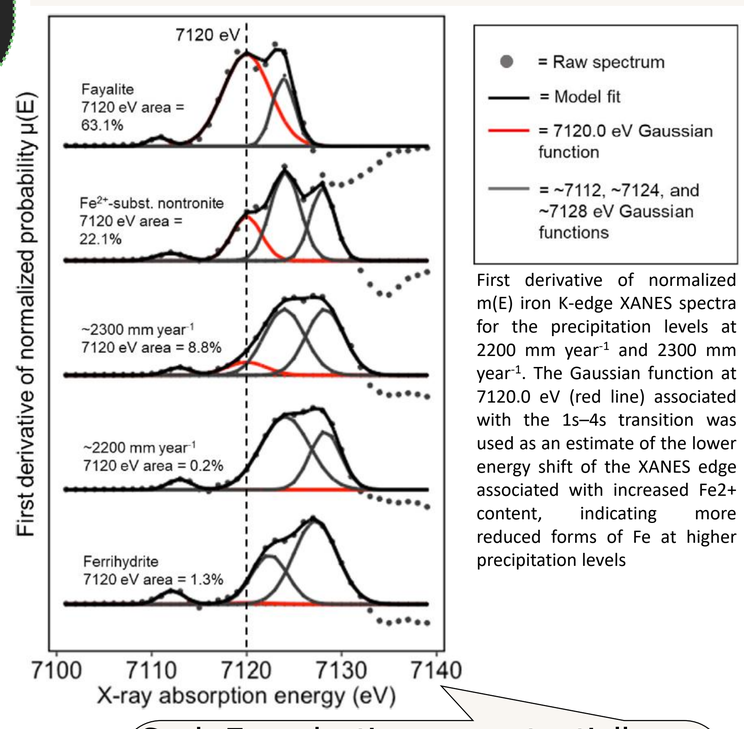
What can we see from bulk soil?

The relative importance of Fe and Al could not be ascertained from only these bulk soil measurements.



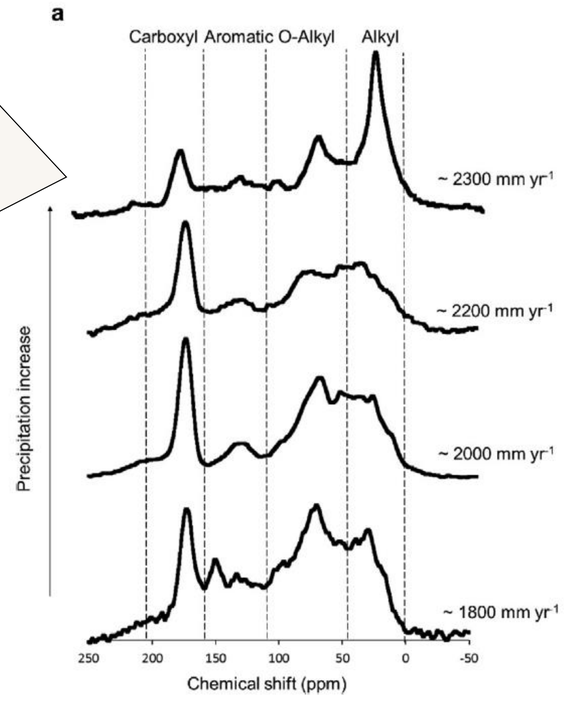
4 Changes in SOC and Fe composition

reduced forms of Fe and lower Carboxylic –C levels at higher precipitation levels



First derivative of normalized m(E) iron K-edge XANES spectra for the precipitation levels at 2200 mm year^{-1} and 2300 mm year^{-1}. The Gaussian function at 7120.0 eV (red line) associated with the 1s–4s transition was used as an estimate of the lower energy shift of the XANES edge associated with increased Fe2+ content, indicating more reduced forms of Fe at higher precipitation levels

The lower proportion of carboxylic C groups at the higher precipitation level may influence organo-mineral associations. Carboxylic C groups play an important role in SOC accrual



^{13}C NMR spectra of the clay fraction (<2 mm) of subsoil samples collected from distinct positions of the climate gradient

Such Fe reduction can potentially result in a loss of SOC to the aqueous phase. Elevated moisture levels can result in SOC losses mainly by its release from Fe associations

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