Allophane Estimation in the Clay Fraction of Volcanic Ash Soils by Rietveld Refinement

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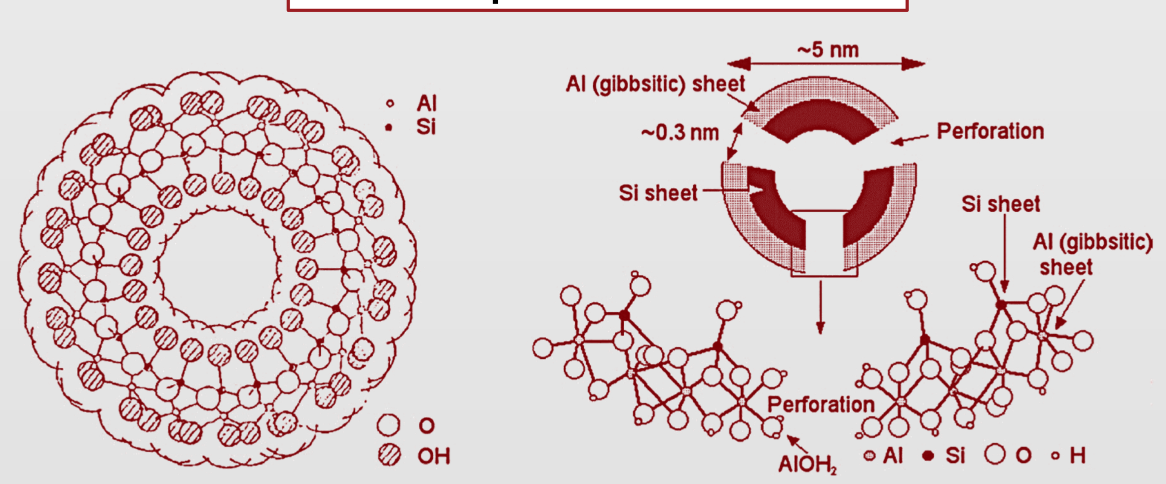
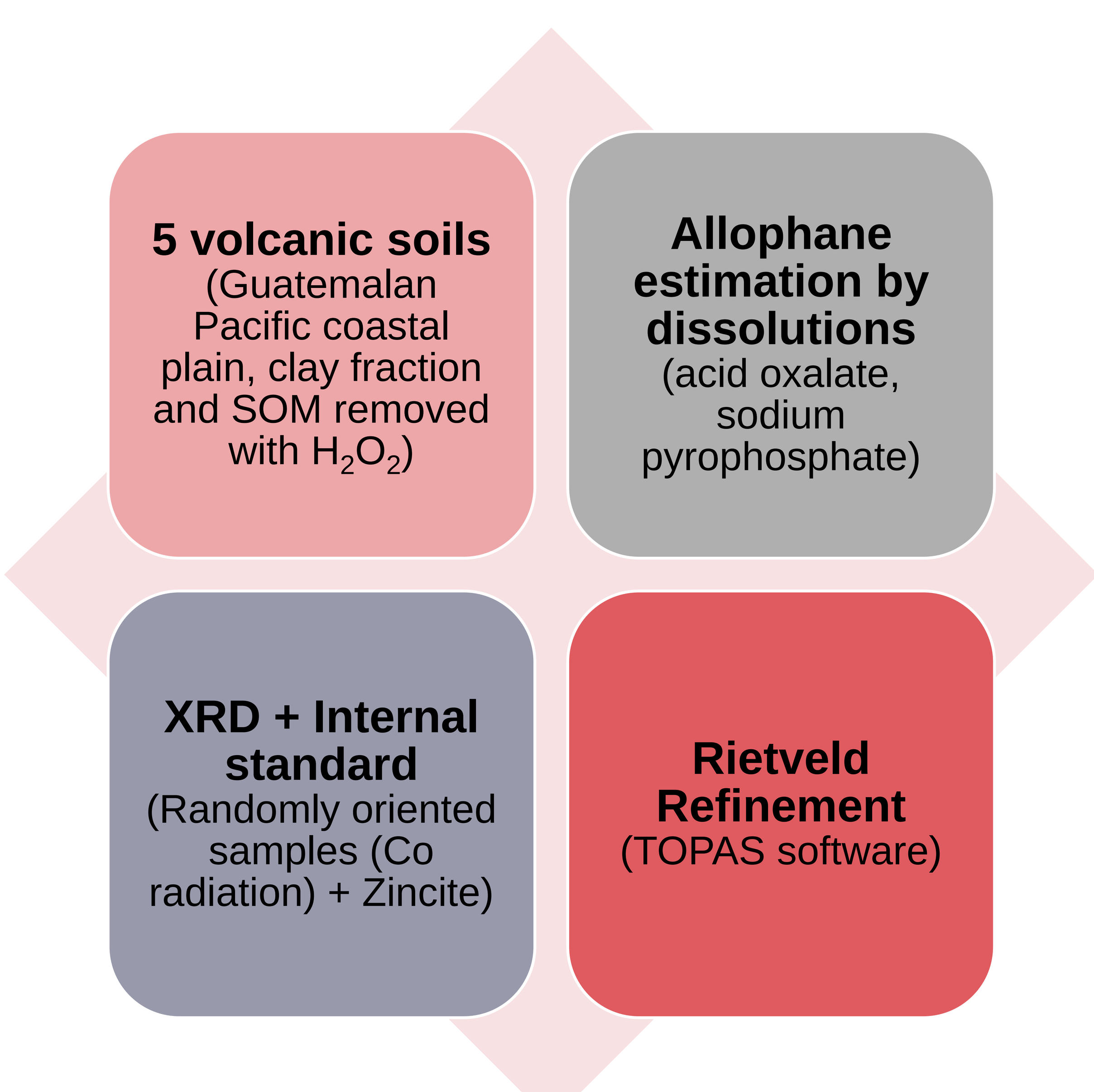
Introduction

- Volcanic ash soil clays
  - dominated by short-range ordered components (allophane)
- Allophane
  - hollow nano-scale spherule structure
  - XR-amorphous, thus quantified by selective dissolution (SD) (oxalate and pyrophosphate)
- SD possibly underestimates allophane in soils
- Rietveld Refinement (RR) method
  - designed to refine unit cell and single crystal coordinates
  - popular minimization technique that employs the kinematic XRD intensity equation: $I_{(2\theta)} = Lp\,|G^2|\,\Phi$
  - uses numerical matrix methods to fit the calculated intensities to observed intensities to quantify full patterns
- TOPAS (*Total Pattern Analysis Solution*) software
  - indirectly estimates amorphous content by RR with internal standard spiking

Allophane structure

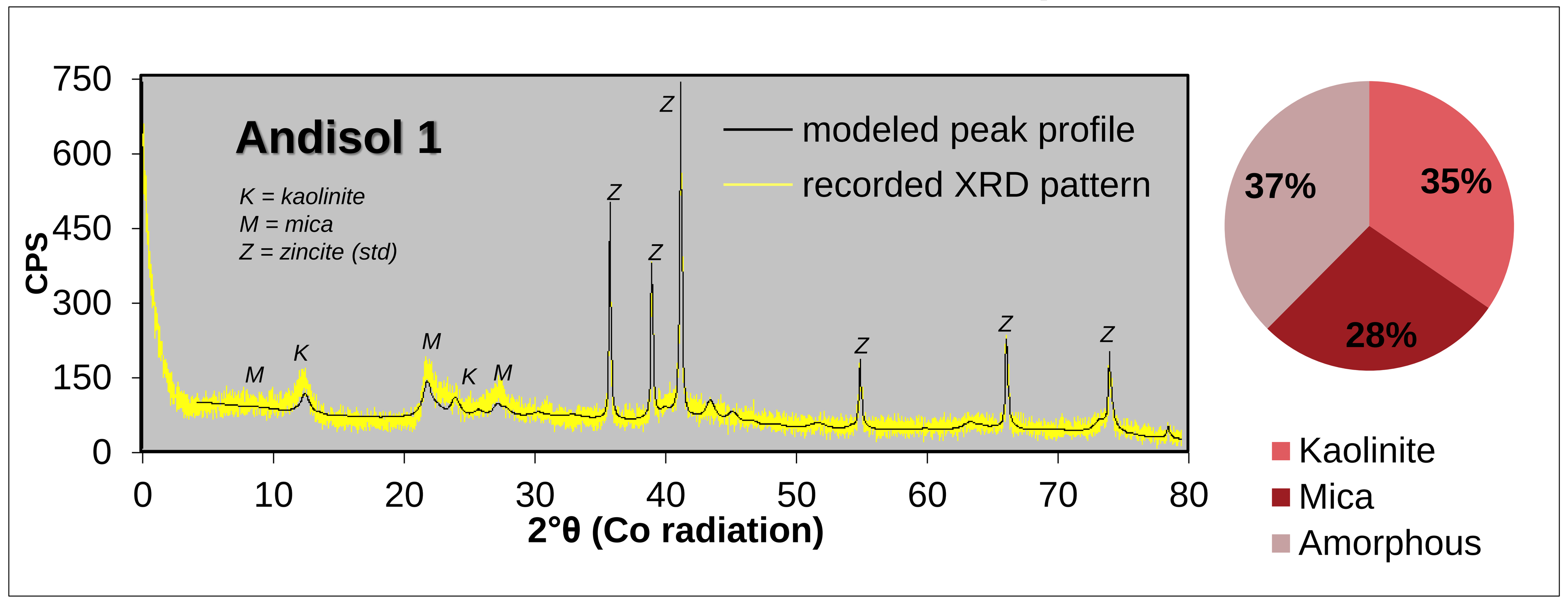


Materials and Methods



Results

Measured and calculated XRD patterns



Allophane estimation by selective dissolutions: $Al_2O_3(SiO_2)_{1.3}{*}2H_2O$

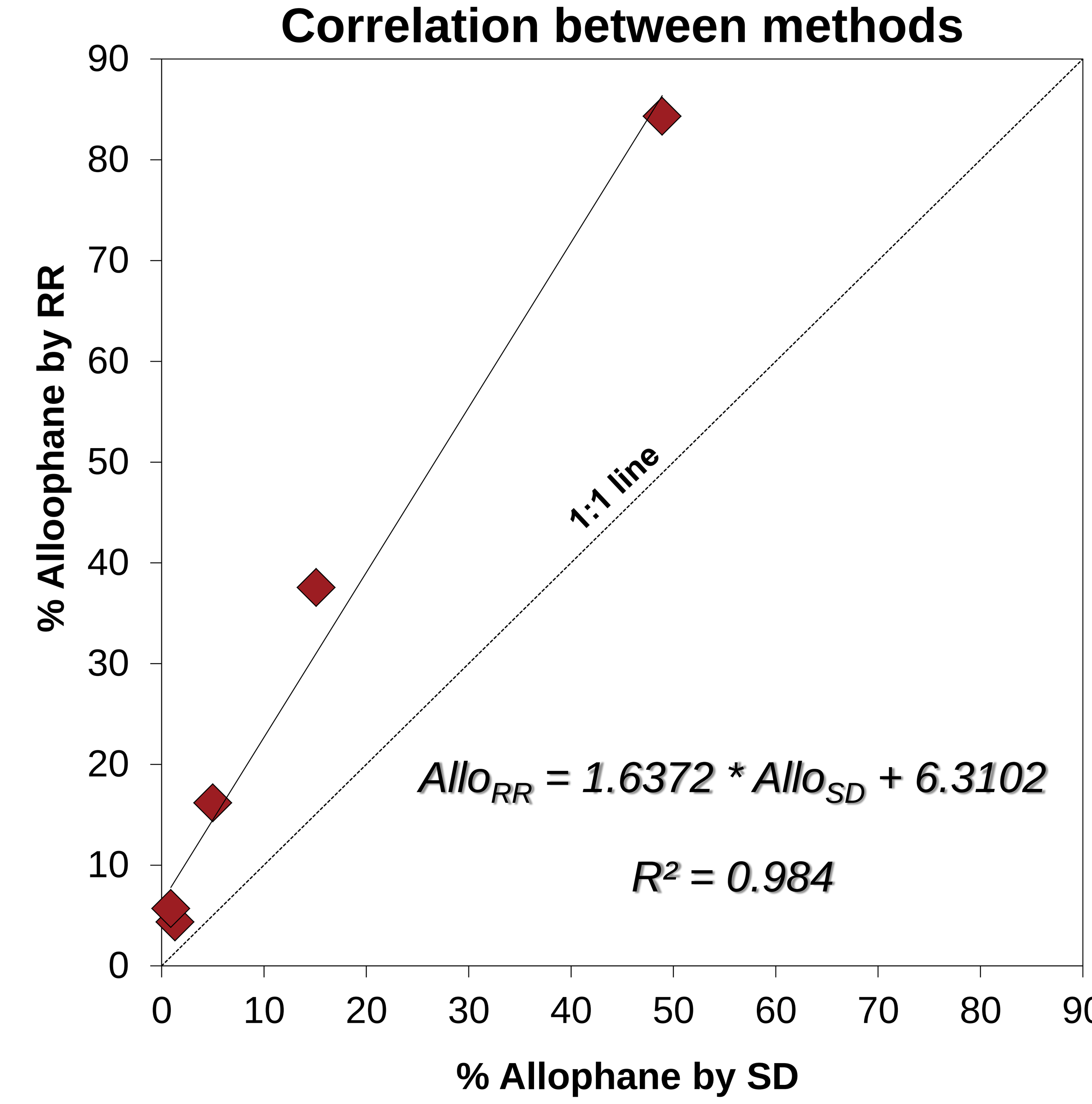
Dissolution	Dissolved phases	Al%	Allophane%
Acid oxalate	Allophane + organically complexed Al	6.5%	**15%**
Pyrophosphate	Organically complexed Al	2.8%	

Allophane estimation by Rietveld Refinement

Soil	Crystalline phases	Amorphous content	R_{wp}*
Andisol 1	Kaolinite: 35% Mica: 28%	**37%**	11.4
Andisol 2	Orthoclase: 1% Mica: 14%	**84%**	12.1
Mollisol	Kaolinite: 39% Sepiolite: 36% Chlorite: 6% Andesine: 3%	**16%**	11.1
Vertisol	Kaolinite: 38% Cristobalite: 23% Smectite: 16% Quartz: 9% Andesine: 4% Halloysite: 3% Mica: 1%	**6%**	11.4
Alfisol	Kaolinite: 44% Mica: 19% Smectite: 32% Palygorskite: 1%	**4%**	11.2

*R_{wp} *(weighted profile R factor): square root of the quantity minimized scaled by the weighted intensities*

Correlation between methods



Implications & Further work

- Quantification of amorphous phases - crucial in understanding reactivity of volcanic ash soils
- Allophane content – governs mineral and contaminant sorption reactions, and accumulation of organic matter
- Further work required with synthetic clay/(allophane, ferrihydrite, imogolite) mixtures to calibrate Rietveld method
- Weighted profile R-factor (R_{wp}) – how good is good enough?

Conclusions

- Allophane by RR linearly correlated with SD
- RR sensitive to differences in extractable allophane
- SD "*underestimates*" allophane content relative to RR

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Selected References

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