Infrared Reflectance Spectroscopy for Detection and Classification of Mineral Components

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Objective of the Study

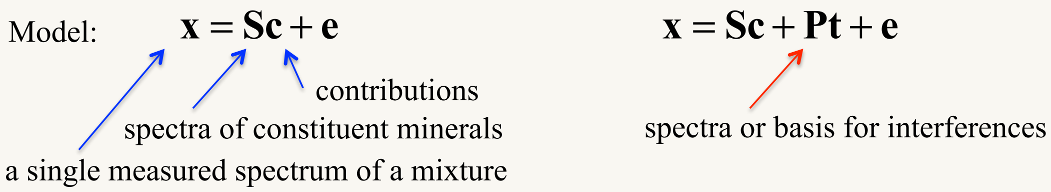
- Proof-of-principle: Can Mid-IR diffuse reflectance spectroscopy be used to separate/differentiate minerals of interest (MOI)?
    - Can it also do so in the presence of ubiquitous interferences?
    - Potentially fast, non-invasive tool for monitoring raw materials in mining applications

Model Calibration & Test

- A Classical Least Squares (CLS) model was calibrated on 22 mixtures of known composition
  - spectra measured at 7490 to 650 cm^{-1} @ 1.4 cm^{-1} increments
  - range of interest: 5500 to 2996, 2829 to 1121cm^{-1}
  - $-\log_{10}(R)$, 1st derivative [SavGol(25,2,1)], 1-Norm
  - XRD (vol %) first guess of contributions
  - Multivariate Curve Resolution (MCR) tuned up the model
- Additional 28 samples available for testing
  - known interferences (no MOI / composition unknown)
  - possible minerals of interest
    - mixtures with low or ~unknown composition

CLS (& ELS)

- Classical least squares (CLS) is a linear mixture model.
- The Extended Mixture Model (Extended Least Squares) can be used to account for interferences.



Model: $\mathbf{x} = \mathbf{S}\mathbf{c} + \mathbf{e}$

contributions

spectra of constituent minerals

a single measured spectrum of a mixture

$\mathbf{x} = \mathbf{S}\mathbf{c} + \mathbf{P}\mathbf{t} + \mathbf{e}$

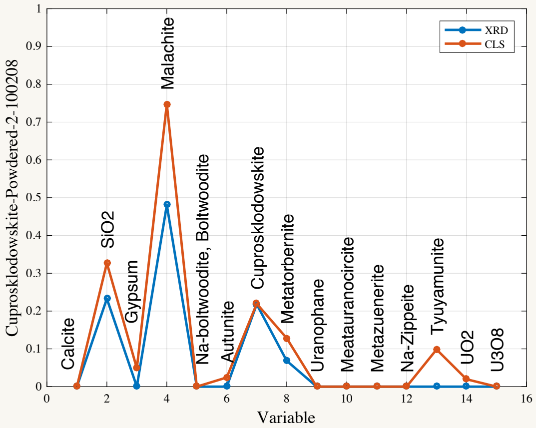
spectra or basis for interferences

Interferences and Minerals of Interest (MOI)

1) Calcite	$CaCO_3$	ubiquitous interference
2) Silica	SiO_2	ubiquitous interference
3) Gypsum	$CaSO_4$•$2(H_2O)$	ubiquitous interference
4) Malachite	$Cu_2(CO_3)(OH)_2$	mineral of interest
5) Na-boltwoodite, Boltwoodite	$(K,Na)(UO_2)(SiO_3OH)$•$1.5(H_2O)$	mineral of interest
6) Autunite	$Ca(UO_2)_2(PO_4)_2$•$6(H_2O)$	mineral of interest - combined w/
Meta-autunite	$Ca(UO_2)_2(PO_4)_2$•$6\text{-}8H_2O$	
7) Cuprosklodowskite	$Cu[(UO_2)(SiO_2OH)]_2$•$6(H_2O)$	mineral of interest
8) Metatorbernite	$Cu(UO_2)_2(PO4)_2$•$8(H_2O)$	mineral of interest
9) Uranophane	$Ca(UO_2)_2SiO_3(OH)_2$•$5(H_2O)$	mineral of interest
10) Meatauranocircite	$Ba(UO_2)_2(PO_4)_2$•$10(H_2O)$	mineral of interest
11) Metazuenerite	$Cu(UO_2)_2(AsO_4)_2$•$8(H_2O)$	mineral of interest
12) Na-Zippeite	$Na_4(UO_2)_6(SO_4)_3(OH)_{10}$•$4(H_2O)$	mineral of interest
13) Tyuyamunite	$Ca(UO_2)_2(VO_4)_2$•$5\text{-}8(H_2O)$	mineral of interest
14) UO2	UO_2	mineral of interest
15) U3O8	U_3O_8	mineral of interest

CLS Model of Mineral Mixtures

Example mixture: Cuprosklodowskite-Powdered-2-100208



- Measured minerals are mixtures of constituent minerals that can be treated as individual chromophores.
- The composition was initially estimated by XRD and 15 major constituents were included in the analysis.

Advantages of CLS

- Contributions and spectra are interpretable
  - signal on interferences and minerals of interest are easily separable
    - statistics can be applied to each source individually
- Can apply non-negativity
  - contributions must all be ≥ 0
  - 1st derivative of the spectra are unconstrained during model identification

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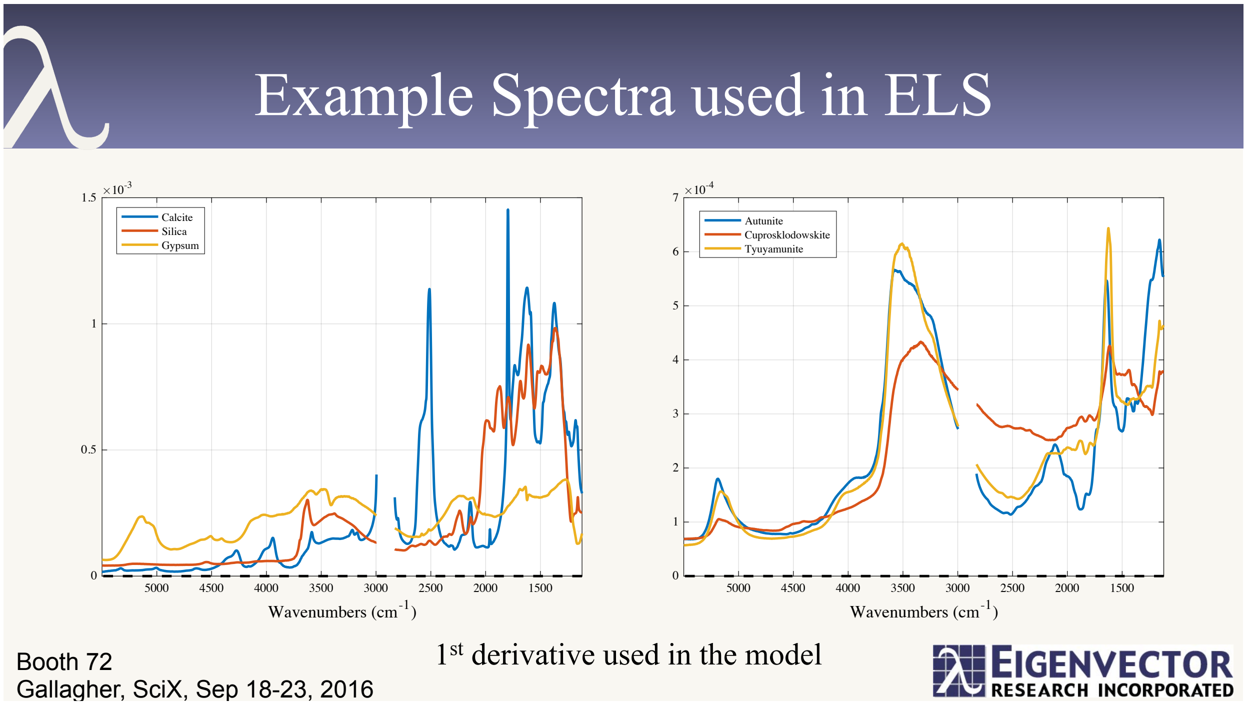

Example Spectra used in ELS

1st derivative used in the model

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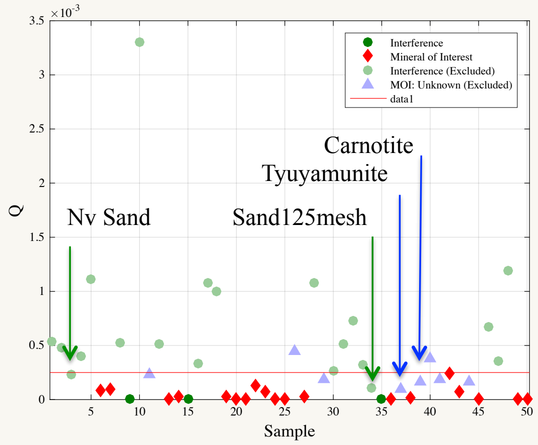
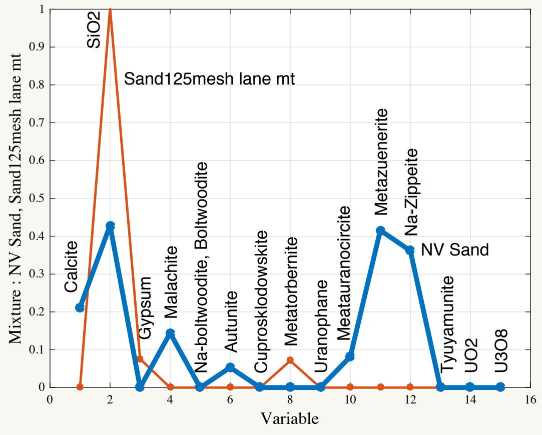
Residuals Analysis



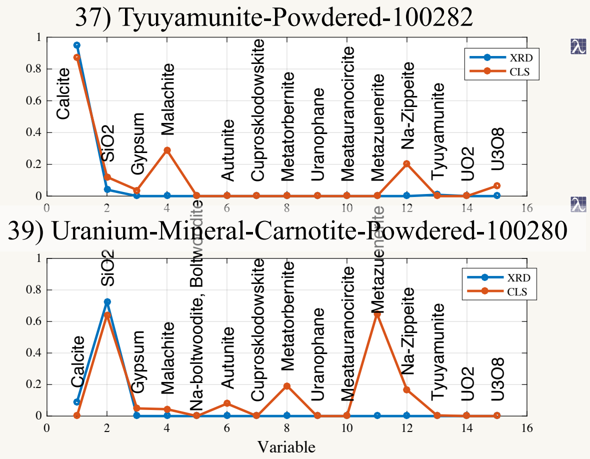
- Two interferences had low residuals:
  - 3) Nv Sand
  - 34) Sand125mesh lane mt
- Six potential MOI had low residuals e.g.,
  - 37) Tyuyamunite-Powdered-100282
  - 39) Uranium-Mineral-Carnotite-Powdered-100280

CLS Contributions for Interferences



- 'Nv Sand' is high in SiO_2 and MOI indicating a possible detection/false alarm
- 'Sand 125 mesh' is high in SiO_2 and is not a false alarm
  - low residual but no contributions on MOI

CLS Contributions for Potential MOI


37) Tyuyamunite-Powdered-100282

39) Uranium-Mineral-Carnotite-Powdered-100280

- ‘Tyuyamunite’ is high in Calcite and possible detection of MOI/false alarm
- ‘Carnotite’ is high in SiO_2 and possible detection of MOI/false alarm

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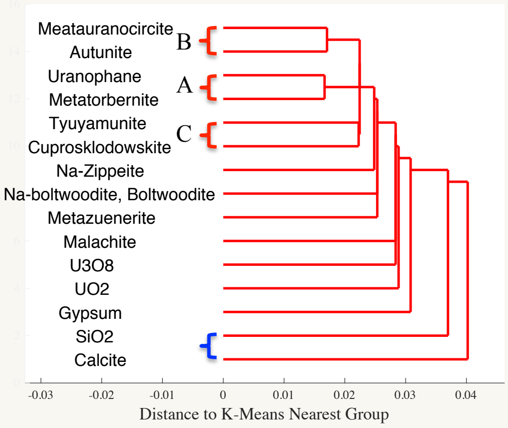
Questions / Future

Dendrogram Using Unscaled Data



- The proof-of-principal was a global model that included 15 factors
- Can sensitivity be improved with local models?
  - hierarchical for models with many analytes and/or
  - specific to task of interest

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Conclusions

- Laboratory study showed that it is possible to use Mid-IR diffuse reflectance spectroscopy to separate/differentiate minerals of interest.
    - 1st derivative was more sensitive and selective than w/o
    - however, preprocessing can be targeted to task of interest
- Augmenting the analysis with NIR may help