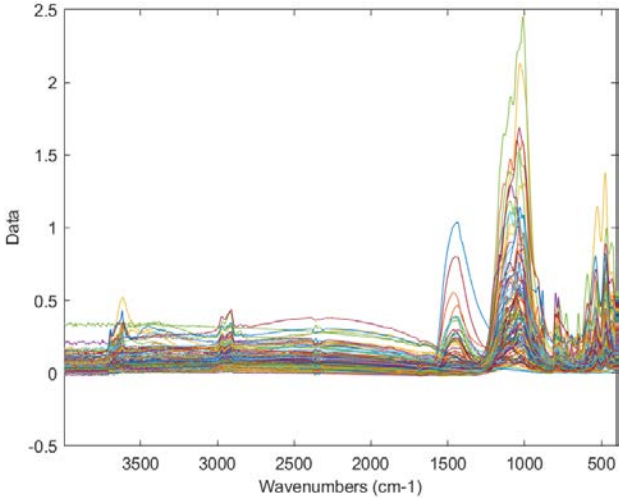
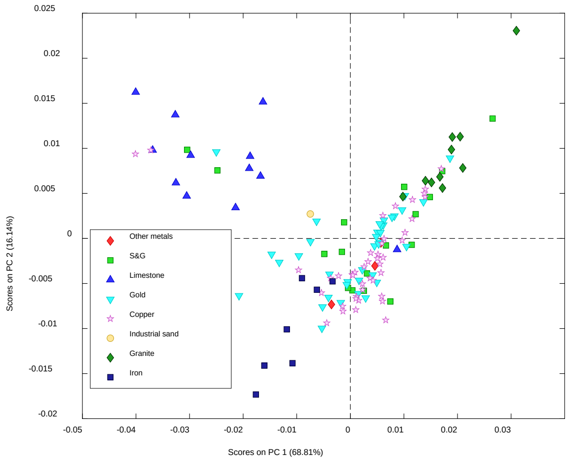
# Advanced Investigation of Mineral Phases Present in Respirable Mine Dust using Principal Components Analysis





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NIOSH-MSHA Respirable Mine Dust Partnership

Silica Exposure and Lung Disease in the Mining Industry Workshop

October 22, 2020

**Pittsburgh Mining Research Division**

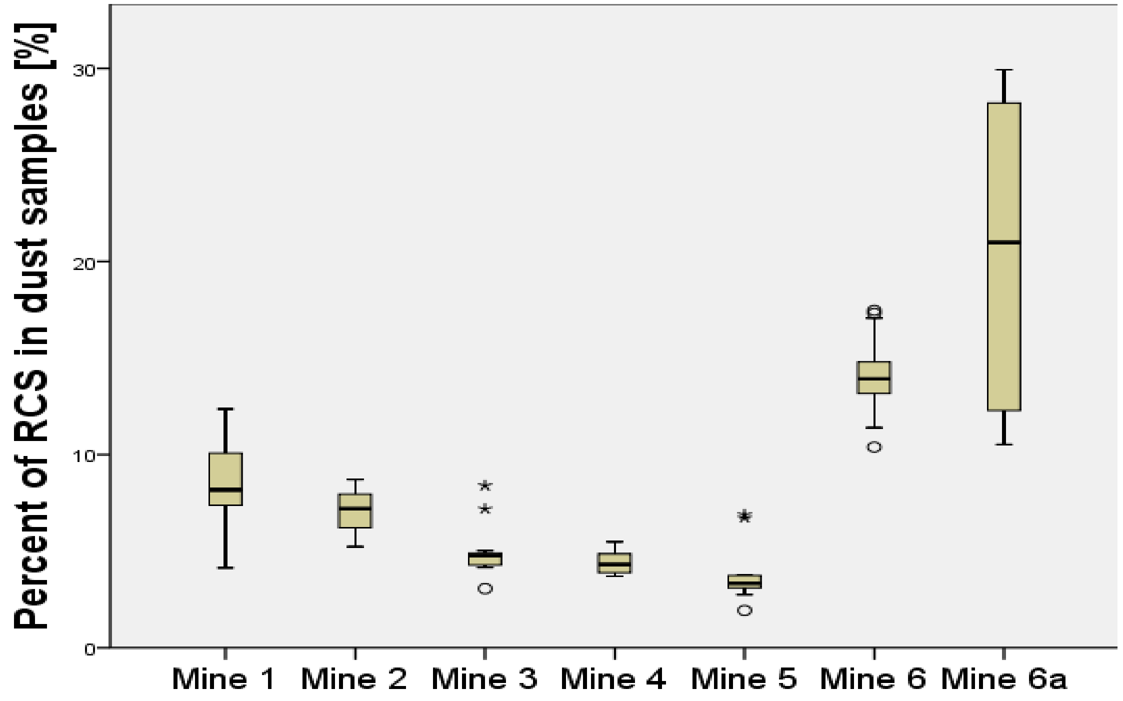
CDC NIOSH

NIOSH Mining Program

# Outline

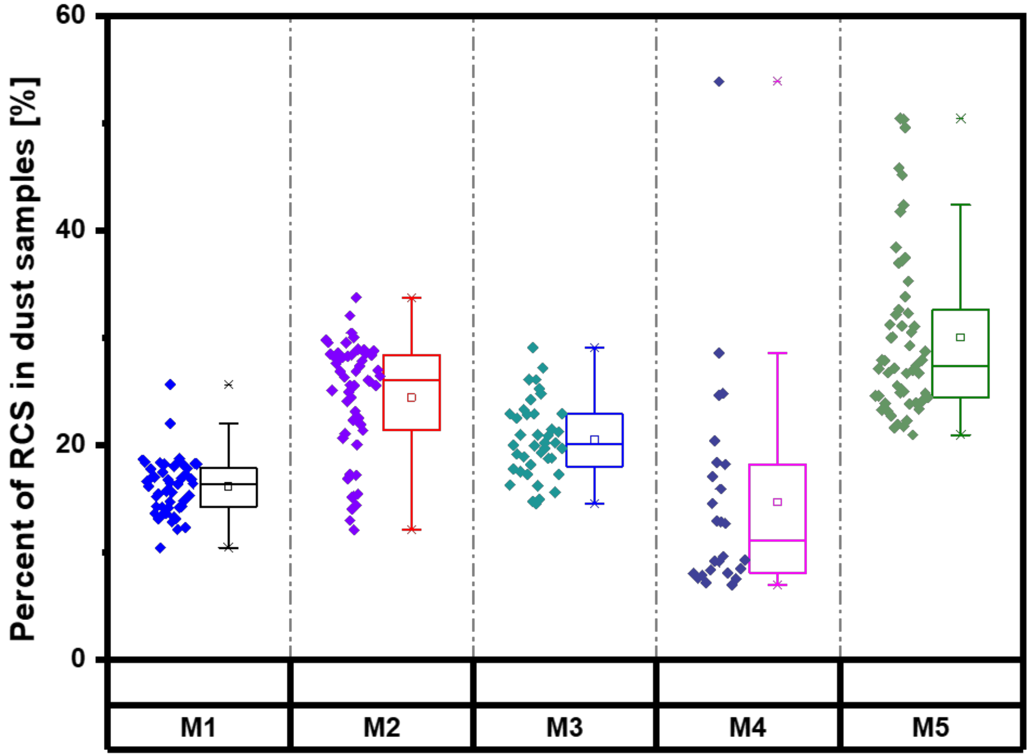
- Variability of respirable crystalline silica (RCS) content
- Variability of other respirable mineral phases
- Methodology
  - Sampling of respirable mine dust
  - X-ray diffraction (XRD) analysis
  - Fourier transform infrared (FTIR) analysis
  - Principal components analysis (PCA) of XRD and FTIR data
- PCA of XRD results
- PCA of FTIR results
- What have we learned?

# Respirable crystalline silica (RCS) can be present in every mining environment




<u>Underground coal mines</u>

*As measured by MSHA P7 and NIOSH 0600 methods*




<u>Five copper mines in AZ and NM – two trips</u>

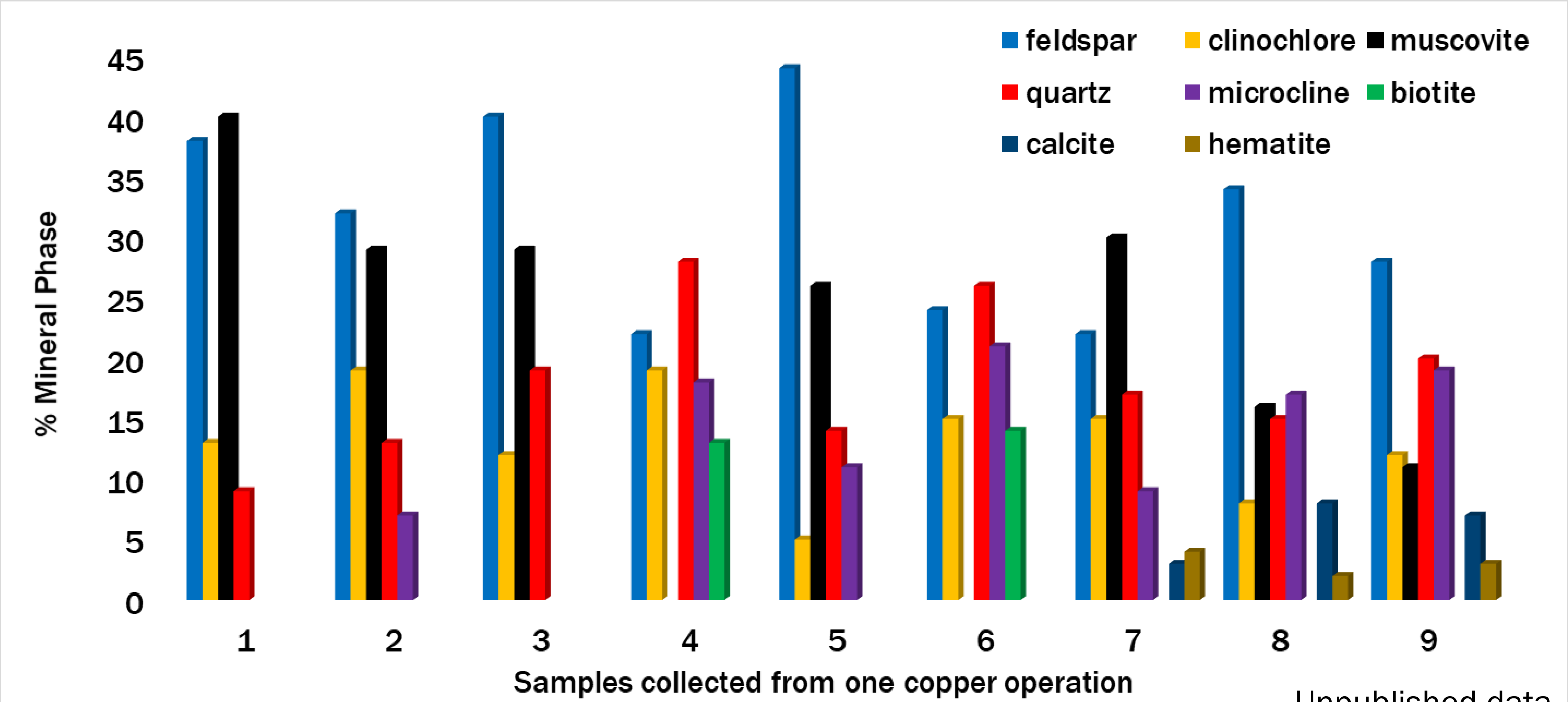
*As measured by NIOSH 7500 and NIOSH 0600 methods*

Miller, A., A. Weakley, P. Griffiths, E. Cauda and S. Bayman (2016). <u>Applied Spectroscopy **71**(5): 1014-1024.</u>

Cauda, E., L. Chubb, R. Reed and R. Stepp (2018). <u>Journal of Occupational and Environmental Hygiene **15**(10): 732-742.</u>

# Advanced exposure monitoring needed that accounts for dust complexity

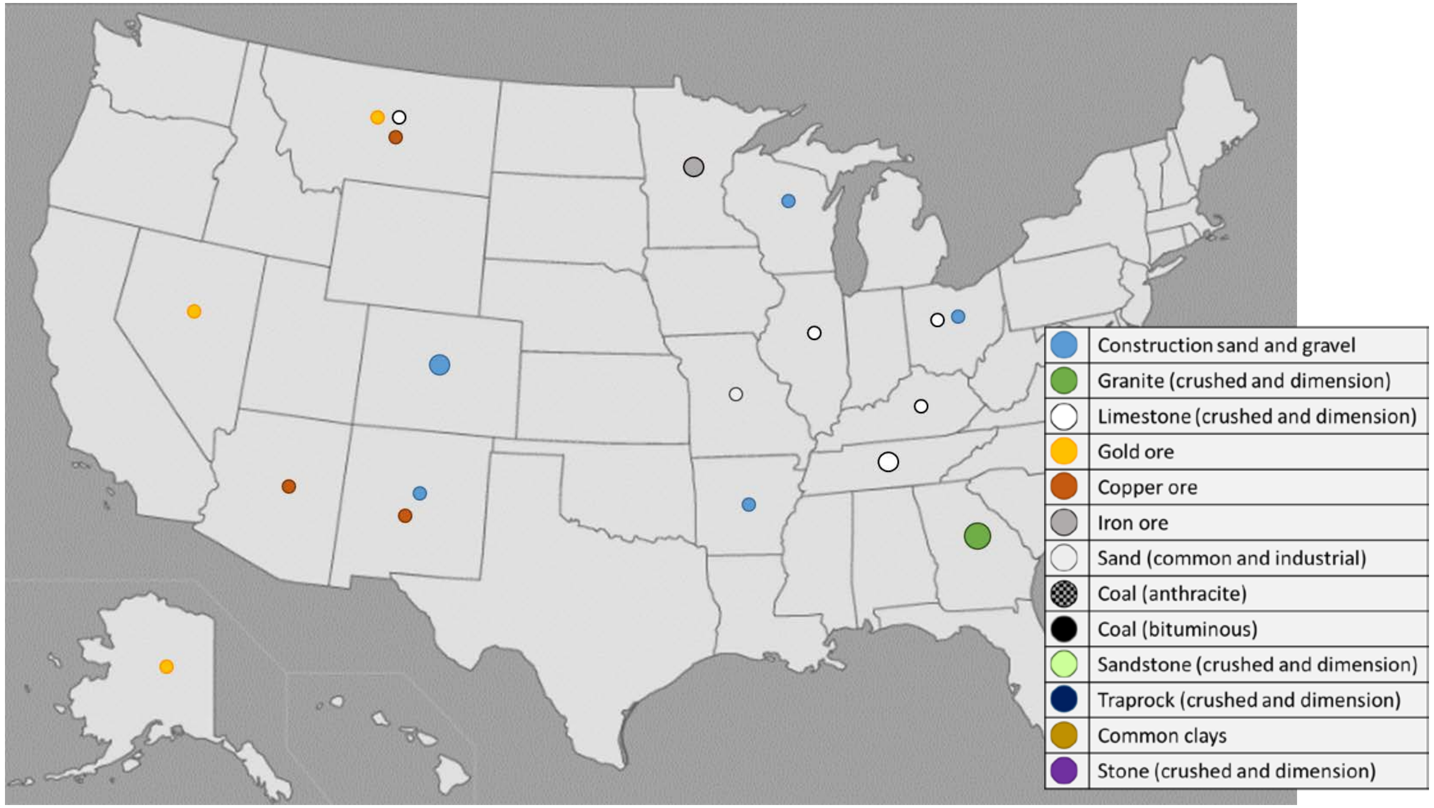
Feldspar minerals, muscovite, microcline are known interferents in the quantification of RCS by FTIR




Unpublished data


# Methodology

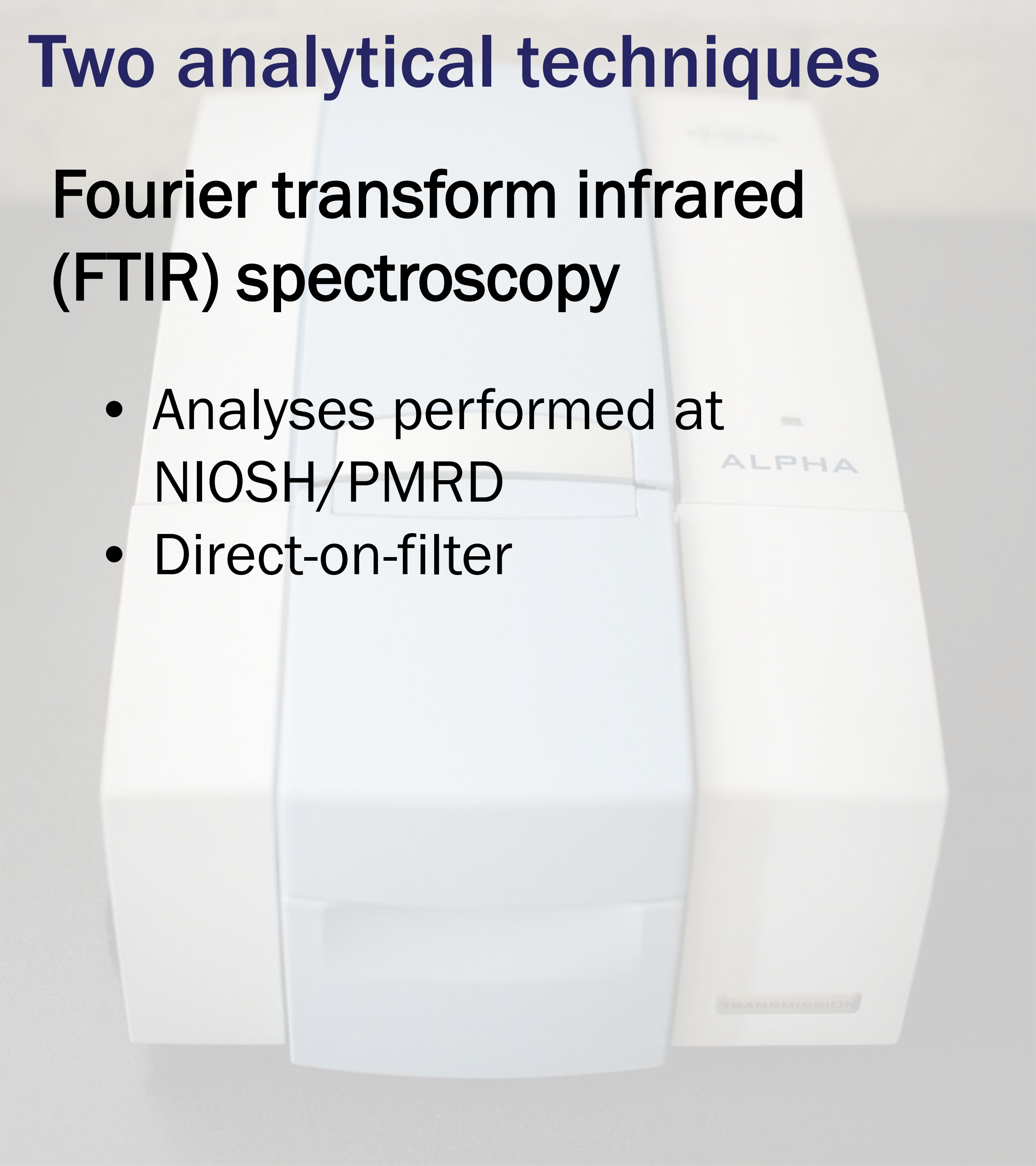
# Sampling of the respirable fraction from bulk material




130 bulk mine dust samples were collected from 57 different operations in 15 different states

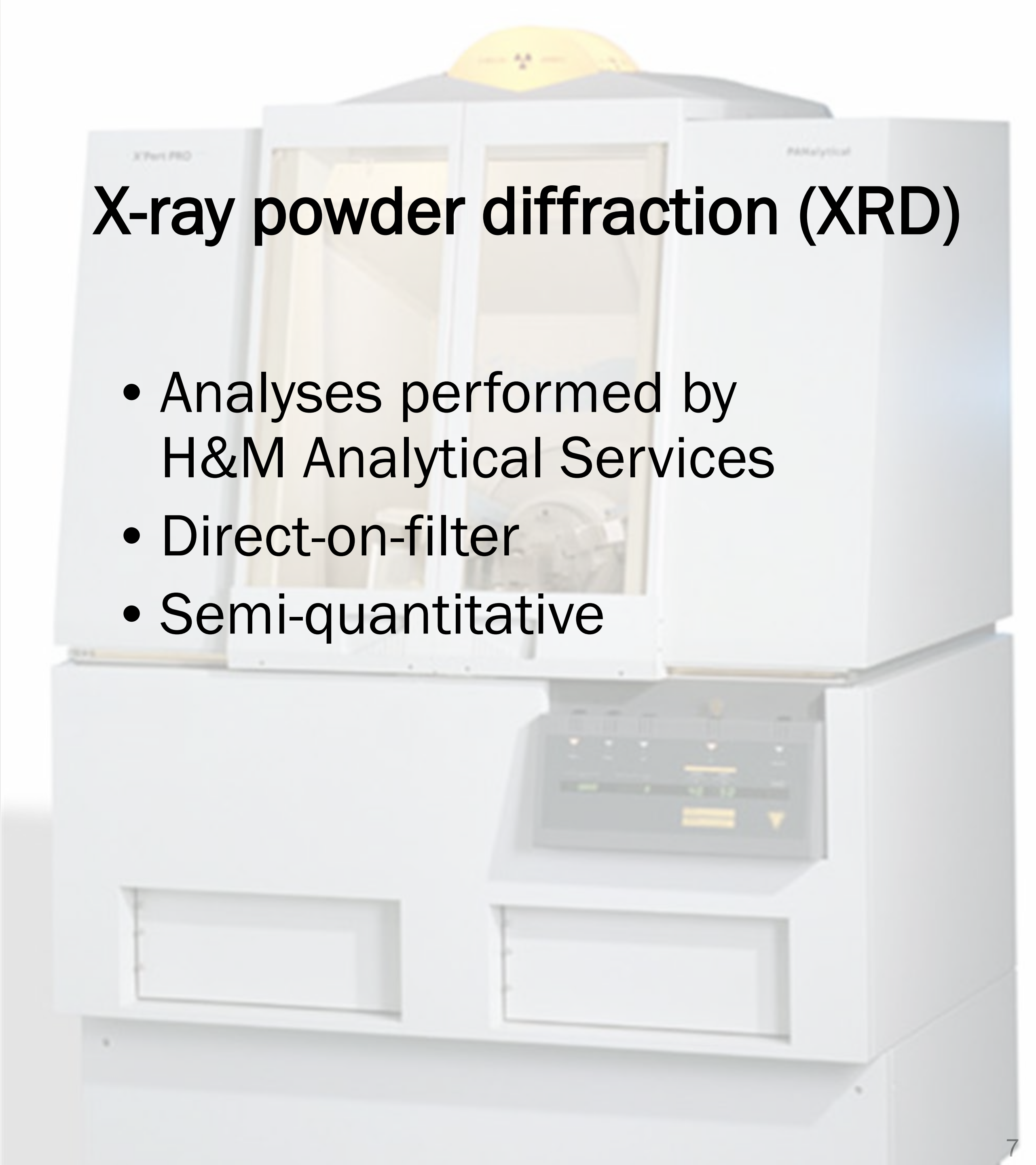
Respirable fraction of each dust is sampled from the bulk material

# Two analytical techniques




## Fourier transform infrared (FTIR) spectroscopy

- Analyses performed at NIOSH/PMRD
- Direct-on-filter



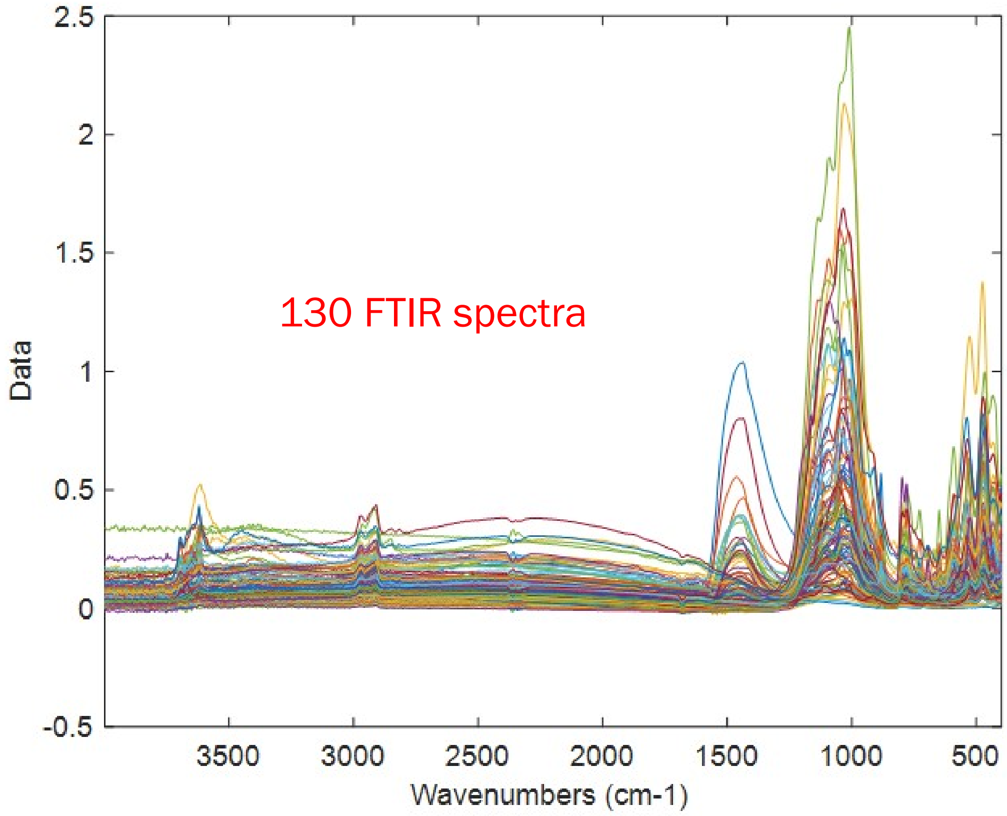
## X-ray powder diffraction (XRD)

- Analyses performed by H&M Analytical Services
- Direct-on-filter
- Semi-quantitative

# Generated a lot of data…

Data table with 130 samples and 29 (possible) mineral phases total

| | Full set | Copper mines | Gold Mines | Iron Mines | Molybdenum mines | Granite mines | S&G mines | Limestone mines |
|---|---|---|---|---|---|---|---|---|
| | *130* | *40* | *36* | *7* | *4* | *11* | *15* | *16* |
| *alpha Quartz* | 100.0% | 100.0% | 100.0% | 100.0% | 100.0% | 100.0% | 100.0% | 100.0% |
| *Cristobalite* | 1.5% | 2.5% | | | | | 6.7% | |
| *Plagioclase* | 66.9% | 92.5% | 72.2% | | 75.0% | 1.0% | 6.0% | 6.3% |
| *K-feldspar* | 56.2% | 77.5% | 36.1% | | 100.0% | 81.8% | 66.7% | 37.5% |
| *Zeolites* | 4.6% | | 8.3% | 42.9% | | | | |
| *Cordierite* | 2.3% | 5.0% | 2.8% | | | | | |
| *Kaolinite* | 25.4% | 32.5% | 2.8% | 85.7% | 100.0% | 36.4% | 33.3% | |
| *Montmorillonite* | 4.6% | 15.0% | | | | | | |
| *Talc* | 2.3% | | 2.8% | 28.6% | | | | |
| *Chlorite* | 44.6% | 65.0% | 52.8% | | | 27.3% | 46.7% | 18.8% |
| *Sepiolite* | 2.3% | | | 42.9% | | | | |
| *Amesite* | 1.5% | | | | | | | 12.5% |
| *Muscovite* | 77.7% | 92.5% | 86.1% | | 100.0% | 63.6% | 53.3% | 81.3% |
| *Biotite* | 3.8% | 5.0% | | | | | 2.0% | |
| *Phlogopite* | 1.5% | | | | | 18.2% | | |
| *Natroapophyllite* | 0.8% | 2.5% | | | | | | |
| *Amphibole* | 6.9% | | 8.3% | 14.3% | | 18.2% | 2.0% | |
| *Calcite* | 40.0% | 45.0% | 27.8% | 14.3% | | 10.0% | 53.3% | 81.3% |
| *Dolomite* | 26.9% | 7.5% | 38.9% | 14.3% | | | 13.3% | 87.5% |
| *Siderite* | 2.3% | | | 42.9% | | | | |
| *Alunite* | 1.5% | 2.5% | 2.8% | | | | | |
| *Jarosite* | 1.5% | | 5.6% | | | | | |
| *Gypusm* | 10.0% | 15.0% | 13.9% | | | | 13.3% | |
| *Apatite* | 1.5% | | | | | | | 6.3% |
| *Hematite* | 7.7% | 12.5% | | 57.1% | | | 6.7% | |
| *Magnetite* | 7.7% | | 11.1% | 85.7% | | | | |
| *Hydroxide* | 3.8% | 2.5% | 2.8% | 42.9% | | | | |
| *Pyrite* | 14.6% | 2.5% | 41.7% | | | | | 18.8% |
| *Unknown* | 7.7% | 5.0% | 5.6% | | | 18.2% | 26.7% | |



# XRD data 29 variables

| | Full set | Copper mines | Gold Mines | Iron Mines | Molybdenum mines | | Granite mines | S&G mines | Limestone mines |
|---|---|---|---|---|---|---|---|---|---|
| | 130 | 40 | 36 | 7 | 4 | | 11 | 15 | 16 |
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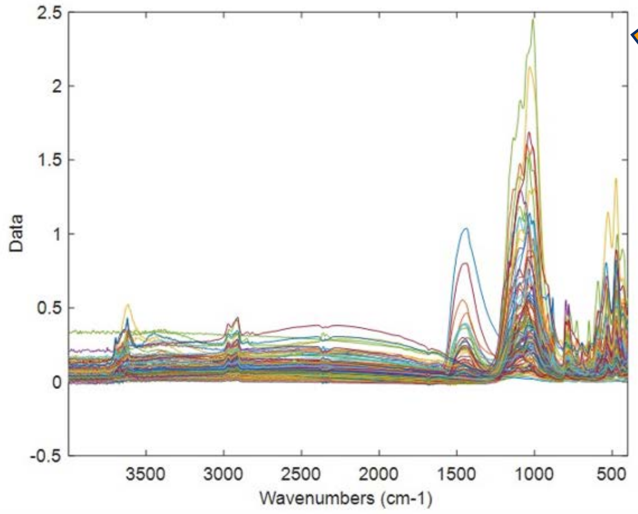
| Chlorite | 44.6% | 65.0% | 52.8% | | | | 27.3% | 46.7% | 18.8% |
| Sepiolite | 2.3% | | | 42.9% | | | | | |
| Amesite | 1.5% | | | | | | | | 12.5% |
| Muscovite | 77.7% | 92.5% | 86.1% | | 100.0% | | 63.6% | 53.3% | 81.3% |
| Biotite | 3.8% | 5.0% | | | | | | 2.0% | |
| Phlogopite | 1.5% | | | | | | 18.2% | | |
| Natroapophyllite | 0.8% | 2.5% | | | | | | | |
| Amphibole | 6.9% | | 8.3% | 14.3% | | | 18.2% | 2.0% | |
| Calcite | 40.0% | 45.0% | 27.8% | 14.3% | | | 10.0% | 53.3% | 81.3% |
| Dolomite | 26.9% | 7.5% | 38.9% | 14.3% | | | | 13.3% | 87.5% |
| Siderite | 2.3% | | | 42.9% | | | | | |
| Alunite | 1.5% | 2.5% | 2.8% | | | | | | |
| Jarosite | 1.5% | | 5.6% | | | | | | |
| Gypsum | 10.0% | 15.0% | 13.9% | | | | | 13.3% | |
| Apatite | 1.5% | | | | | | | | 6.3% |
| Hematite | 7.7% | 12.5% | | 57.1% | | | | 6.7% | |
| Magnetite | 7.7% | | 11.1% | 85.7% | | | | | |
| Hydroxide | 3.8% | 2.5% | 2.8% | 42.9% | | | | | |
| Pyrite | 14.6% | 2.5% | 41.7% | | | | | | 18.8% |
| Unknown | 7.7% | 5.0% | 5.6% | | | | 18.2% | 26.7% | |

# OR

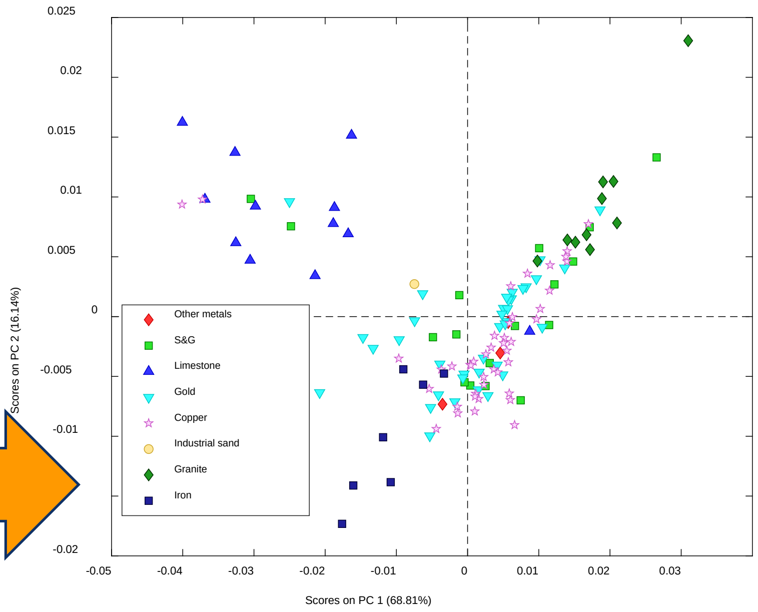
# FTIR data 1765 variables




Mathematical technique

# Principal Components Analysis (PCA)

(MATLAB + PLS_Toolbox)




- Provides better visualization
- Maximizes relevant information
- Reveals patterns and unique samples

# General process for Principal Components Analysis

## 1. Examine data

| | Full set | Copper mines | Gold Mines | Iron Mines | Molybdenum mines | Granite mines | S&G mines | Limestone mines |
|---|---|---|---|---|---|---|---|---|
| | 130 | 40 | 36 | 7 | 4 | 11 | 15 | 16 |
| alpha Quartz | 100.0% | 100.0% | 100.0% | 100.0% | 100.0% | 100.0% | 100.0% | 100.0% |
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| Biotite | 3.8% | 5.0% | | | | | 2.0% | |
| Phlogopite | 1.5% | | | | | 18.2% | | |
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| Amphibole | 6.9% | | 8.3% | 14.3% | | 18.2% | 2.0% | |
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| Siderite | 2.3% | | | 42.9% | | | | |
| Alunite | 1.5% | 2.5% | 2.8% | | | | | |
| Jarosite | 1.5% | | 5.6% | | | | | |
| Gypsum | 10.0% | 15.0% | 13.9% | | | | 13.3% | |
| Apatite | 1.5% | | | | | | | 6.3% |
| Hematite | 7.7% | 12.5% | | 57.1% | | | 6.7% | |
| Magnetite | 7.7% | | 11.1% | 85.7% | | | | |
| Hydroxide | 3.8% | 2.5% | 2.8% | 42.9% | | | | |
| Pyrite | 14.6% | 2.5% | 41.7% | | | | | 18.8% |
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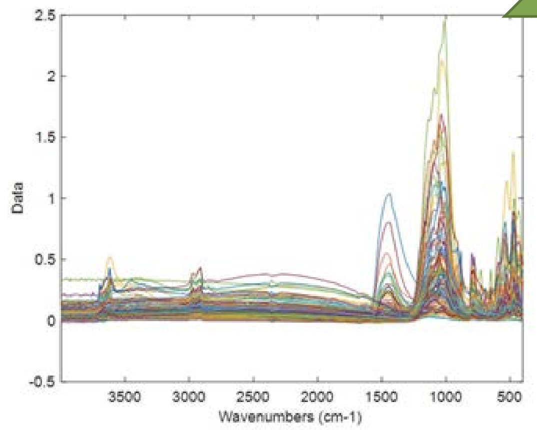
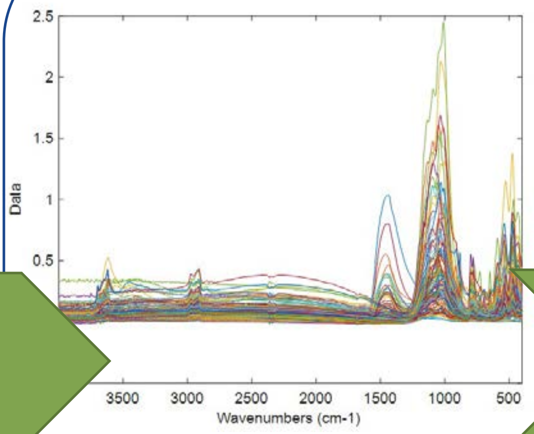
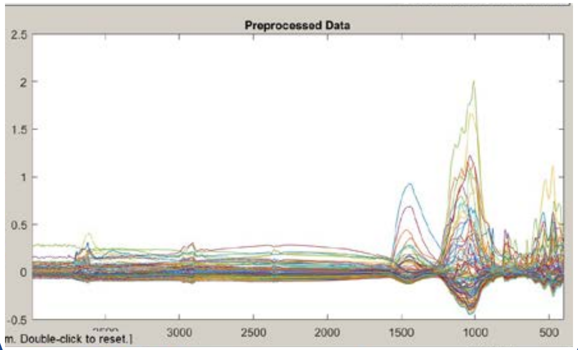



## 2. Pre-process

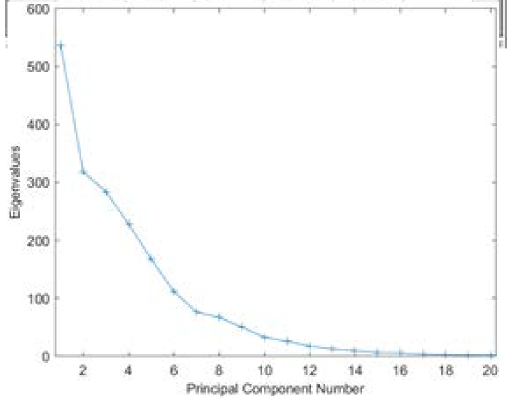


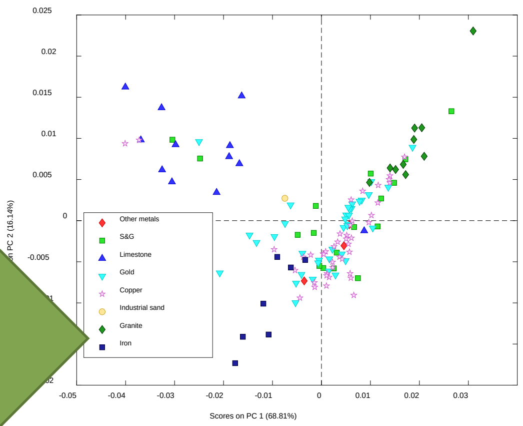

## 3. Estimate model

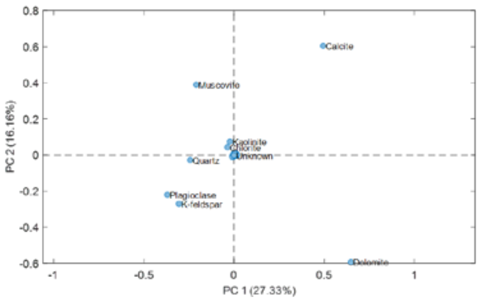
Percent Variance Captured by PCA Model (* = suggested)

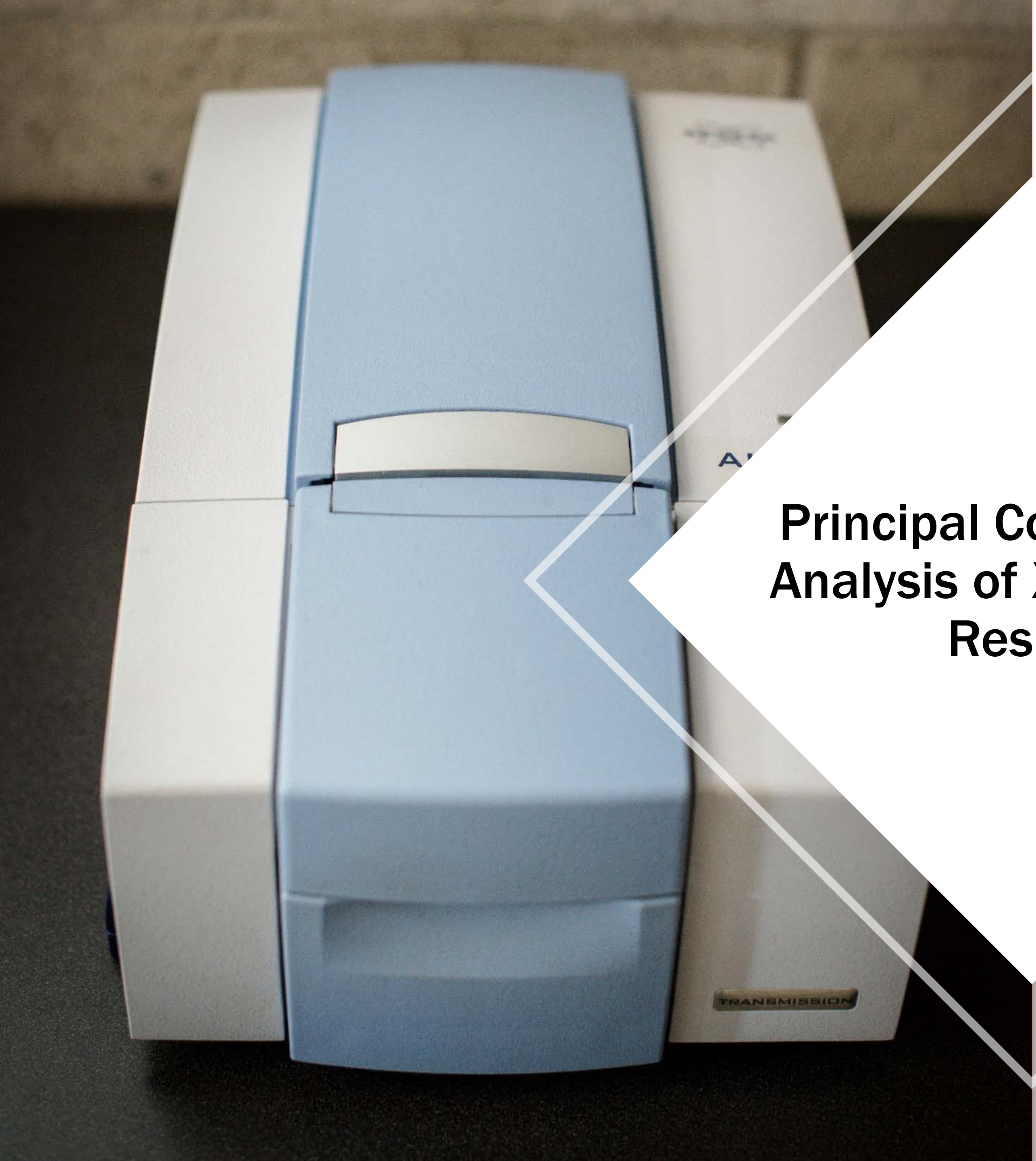
| | Eigenvalu of Cov(X) | % Variance | % Varian Cumulati | RMSEC | RMSECV | |
|---|---|---|---|---|---|---|
| 1 | 5.37e+... | 27.33 | 27.33 | 6.992 | 8.725 | current* |
| 2 | 3.18e+... | 16.16 | 43.49 | 6.165 | 9.358 | |
| 3 | 2.84e+... | 14.43 | 57.92 | 5.32 | 12.73 | |
| 4 | 2.29e+... | 11.63 | 69.55 | 4.526 | 14.05 | |
| 5 | 1.68e+... | 8.54 | 78.09 | 3.839 | 13.11 | |
| 6 | 1.12e+... | 5.68 | 83.76 | 3.305 | 16.99 | |
| 7 | 7.64e+... | 3.89 | 87.65 | 2.882 | 21.06 | |
| 8 | 6.75e+... | 3.43 | 91.08 | 2.449 | 27.38 | |
| 9 | 5.06e+... | 2.57 | 93.66 | 2.066 | 26.74 | |
| 10 | 3.29e+... | 1.68 | 95.33 | 1.772 | 42.65 | |
| 11 | 2.62e+... | 1.33 | 96.66 | 1.498 | 63.32 | |
| 12 | 1.79e+... | 0.91 | 97.58 | 1.277 | 68.77 | |
| 13 | 1.25e+... | 0.64 | 98.21 | 1.096 | 76.35 | |
| 14 | 9.93e+... | 0.51 | 98.72 | 0.9284 | 88.9 | |
| 15 | 6.55e+... | 0.33 | 99.05 | 0.7987 | 106 | |



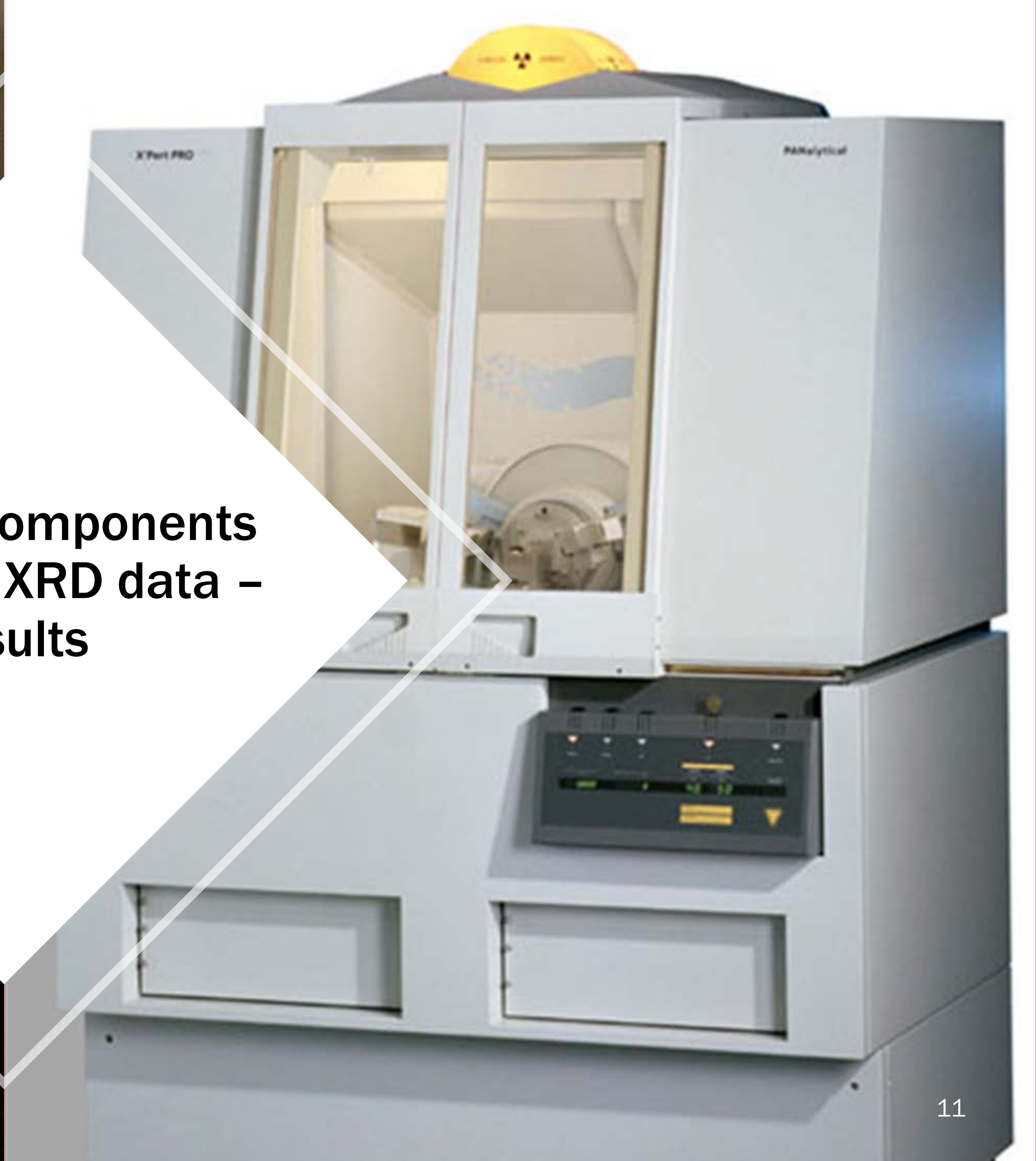

## 4. Examine model



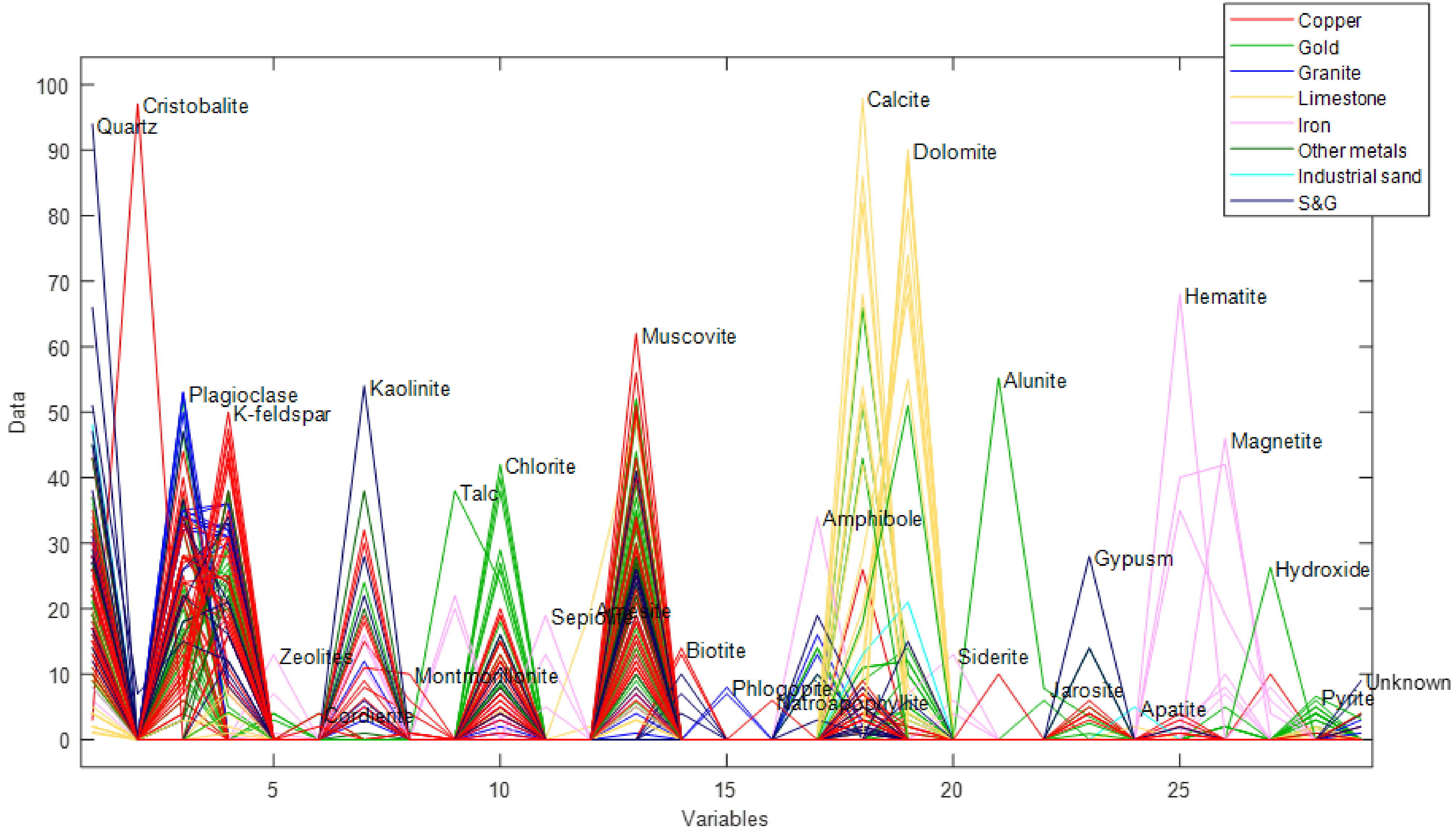






# Principal Components Analysis of XRD data – Results



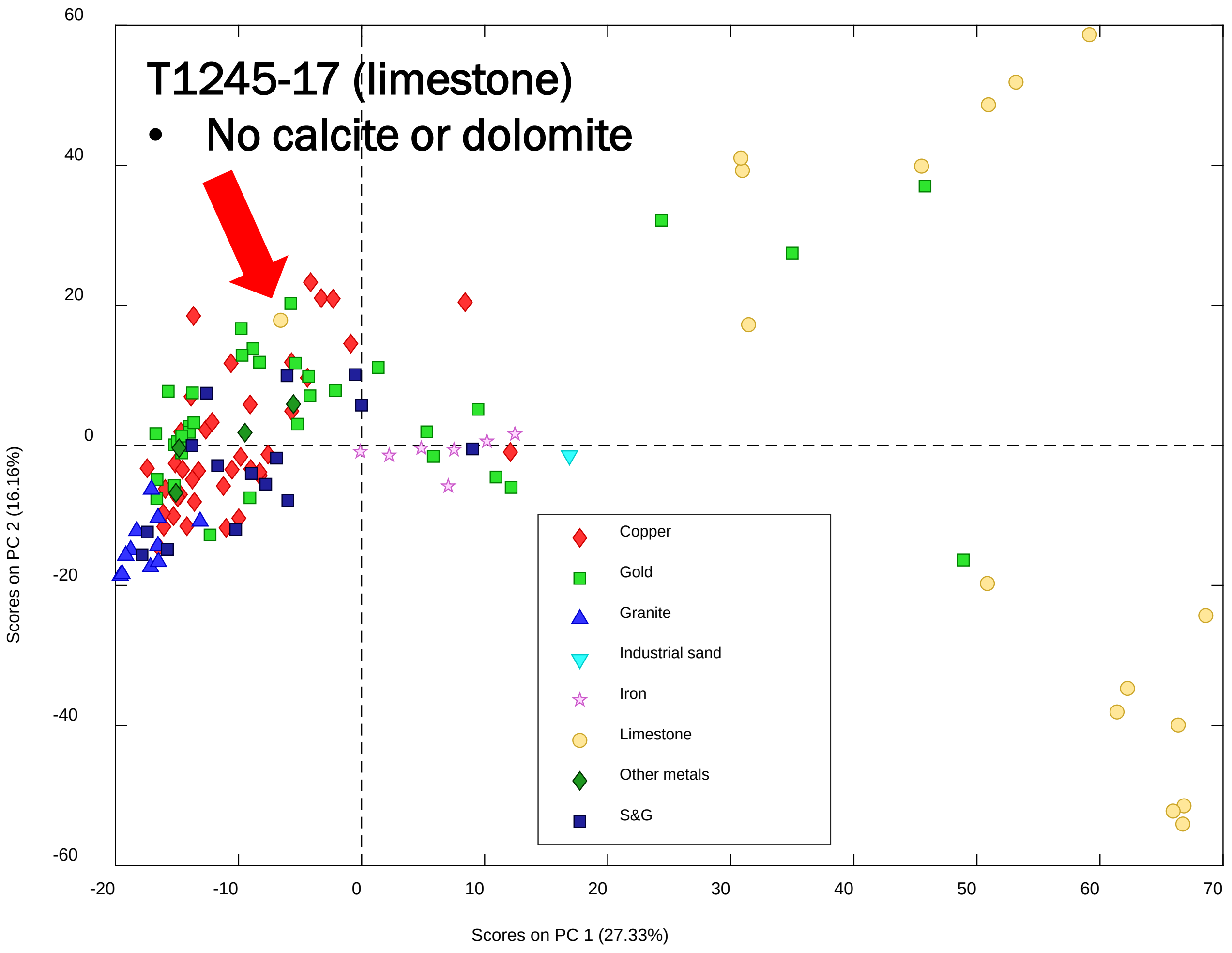
# Complexity of mine dusts – XRD perspective



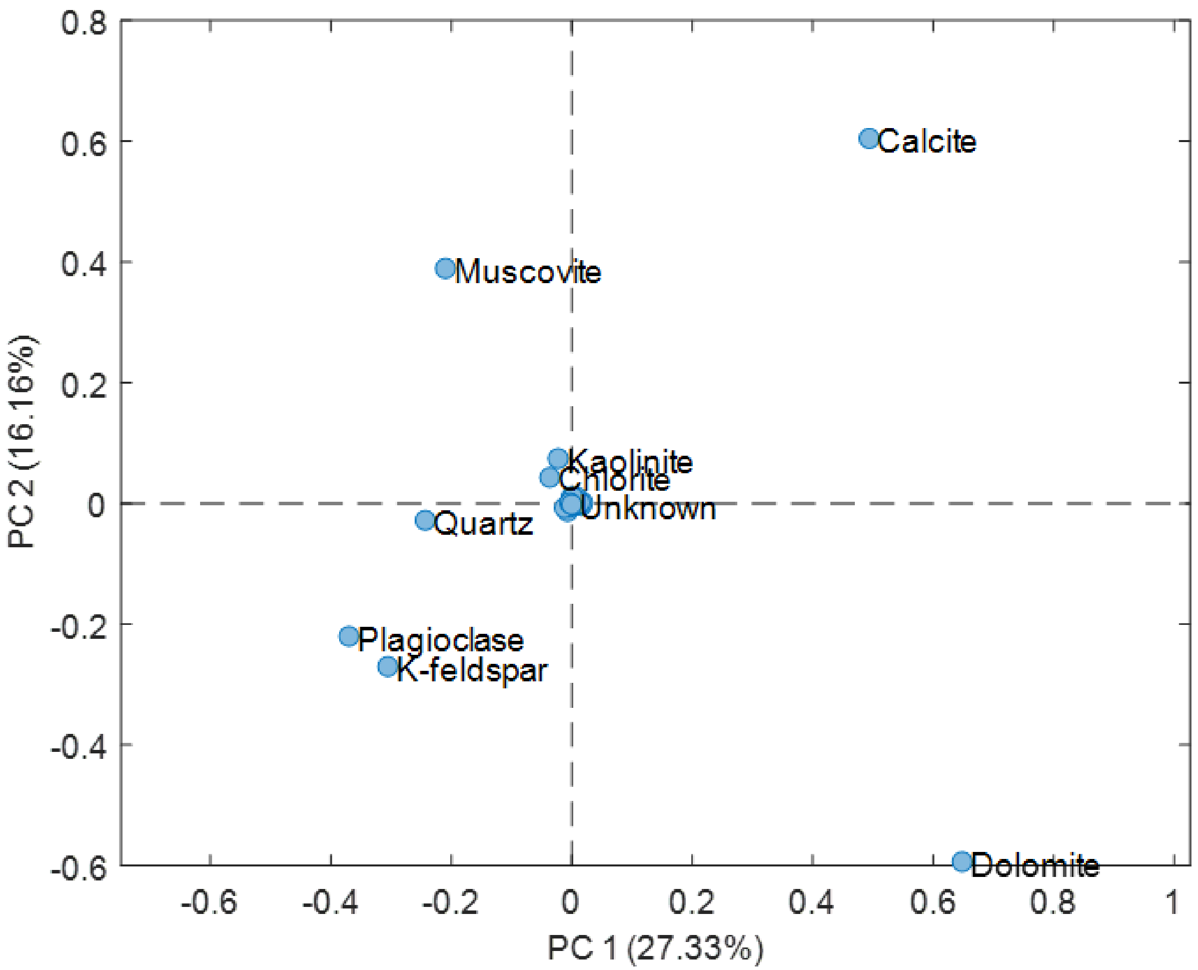

Abundance of mineral phases in samples collected from different mining operations

# Principal Components Analysis of XRD Data

## Scores and Loadings plots



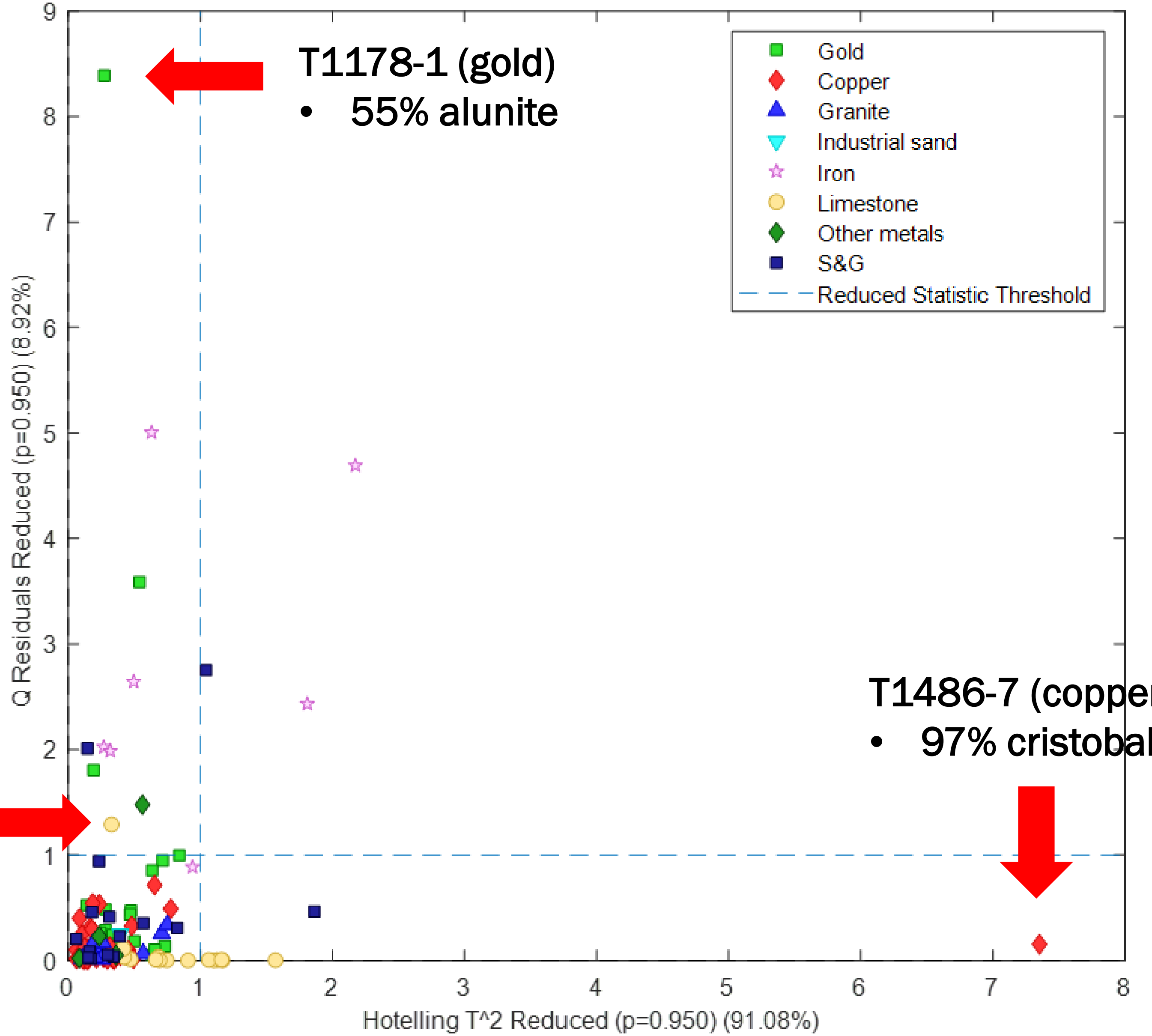

Relationships between samples: limestone samples show strong similarity with each other within the model




Relationships between variables: dolomite, calcite and muscovite are strongly influential to the model

# Principal Components Analysis of XRD Data

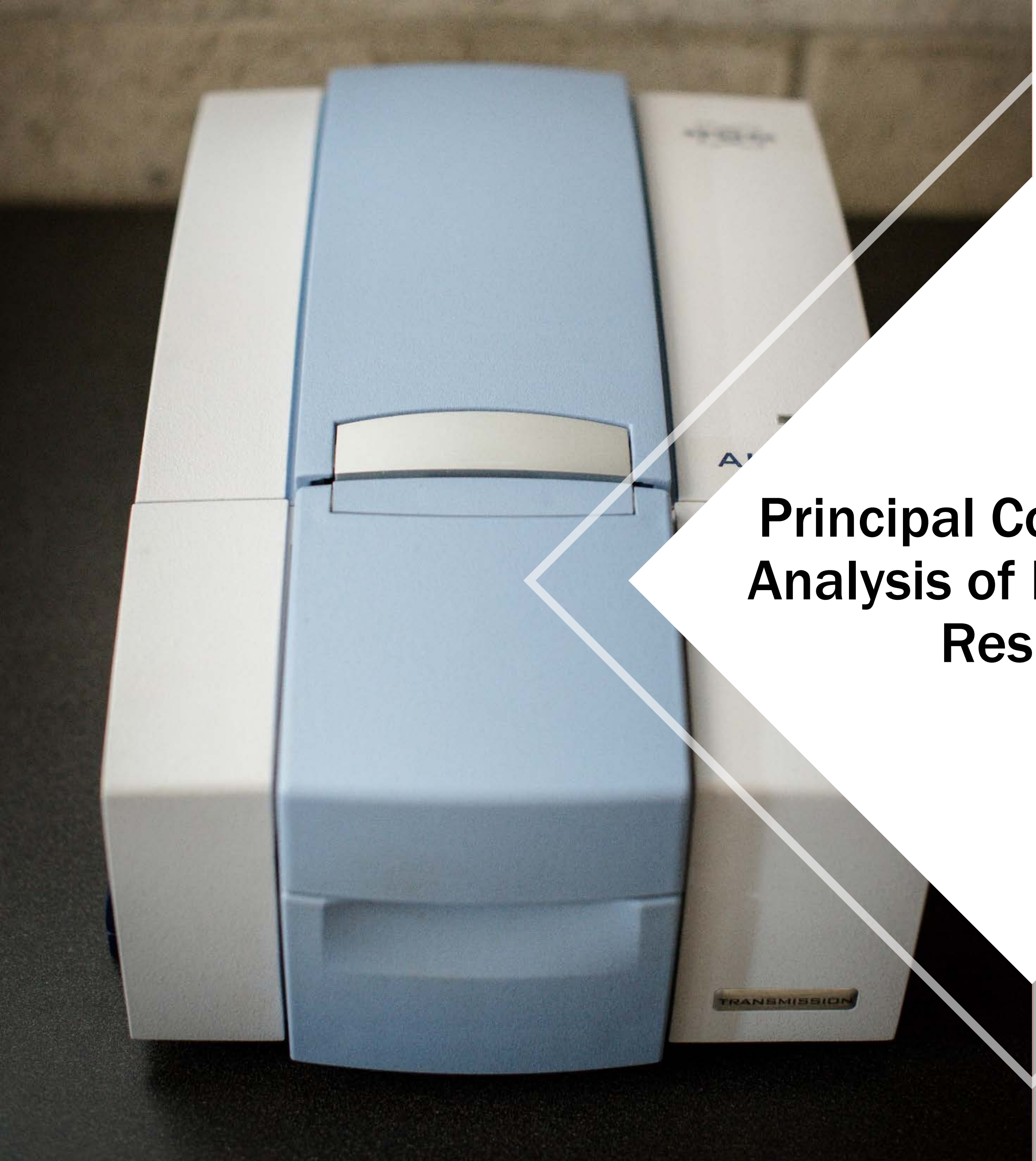
## Identification of unique samples



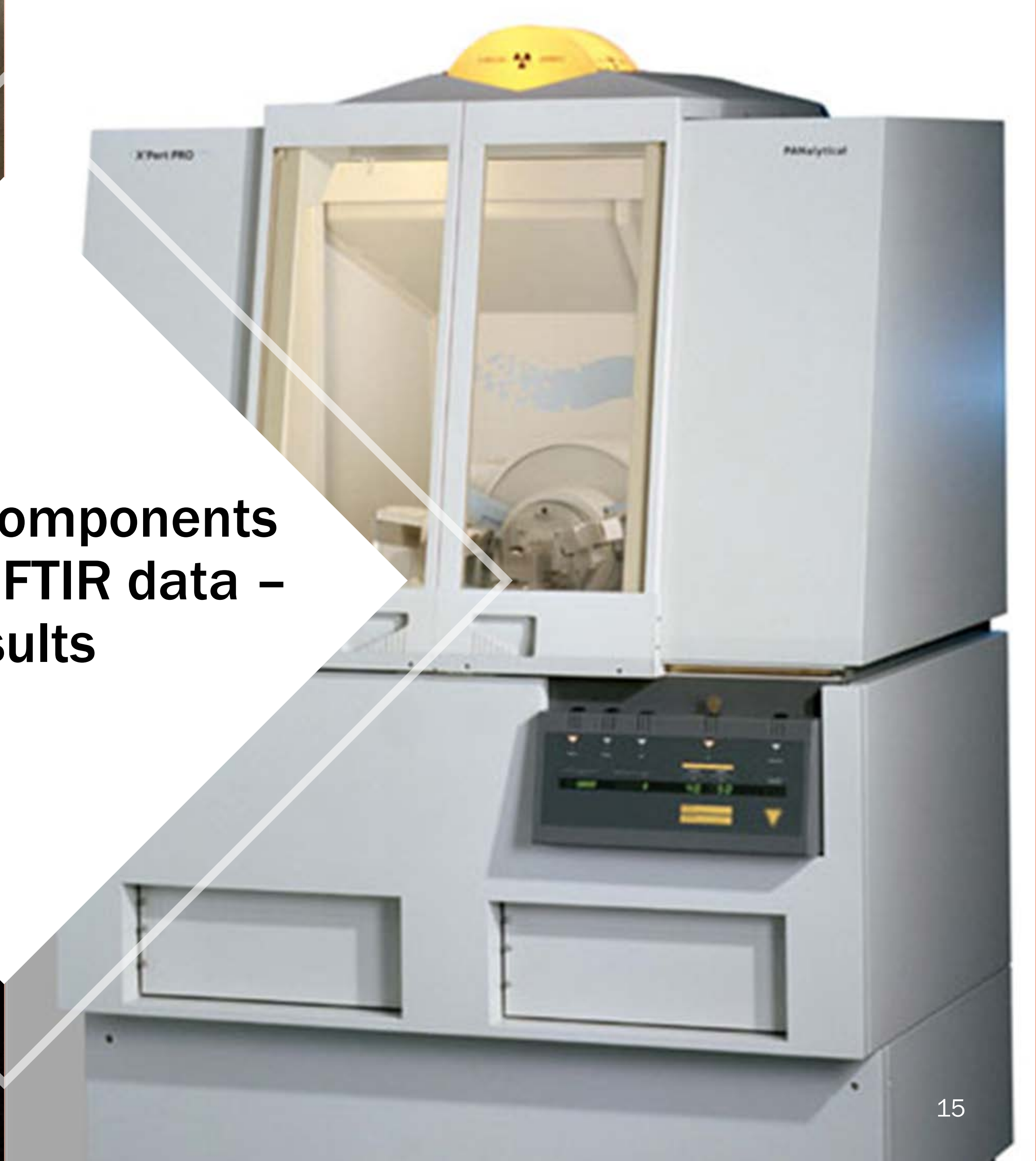

T1178-1 (gold)
- 55% alunite

T1486-7 (copper)
- 97% cristobalite

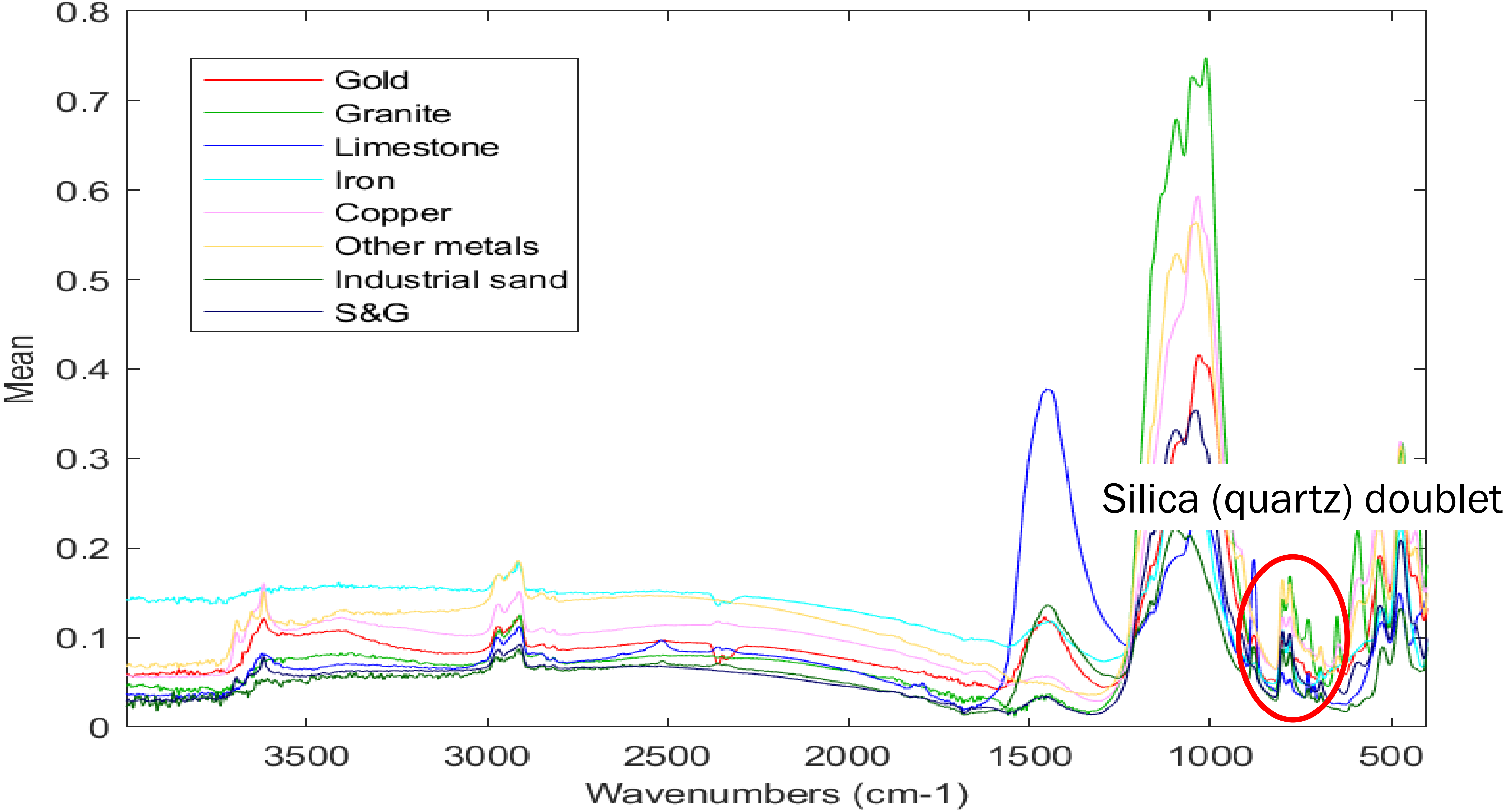
T1245-17 (limestone)
- No calcite or dolomite



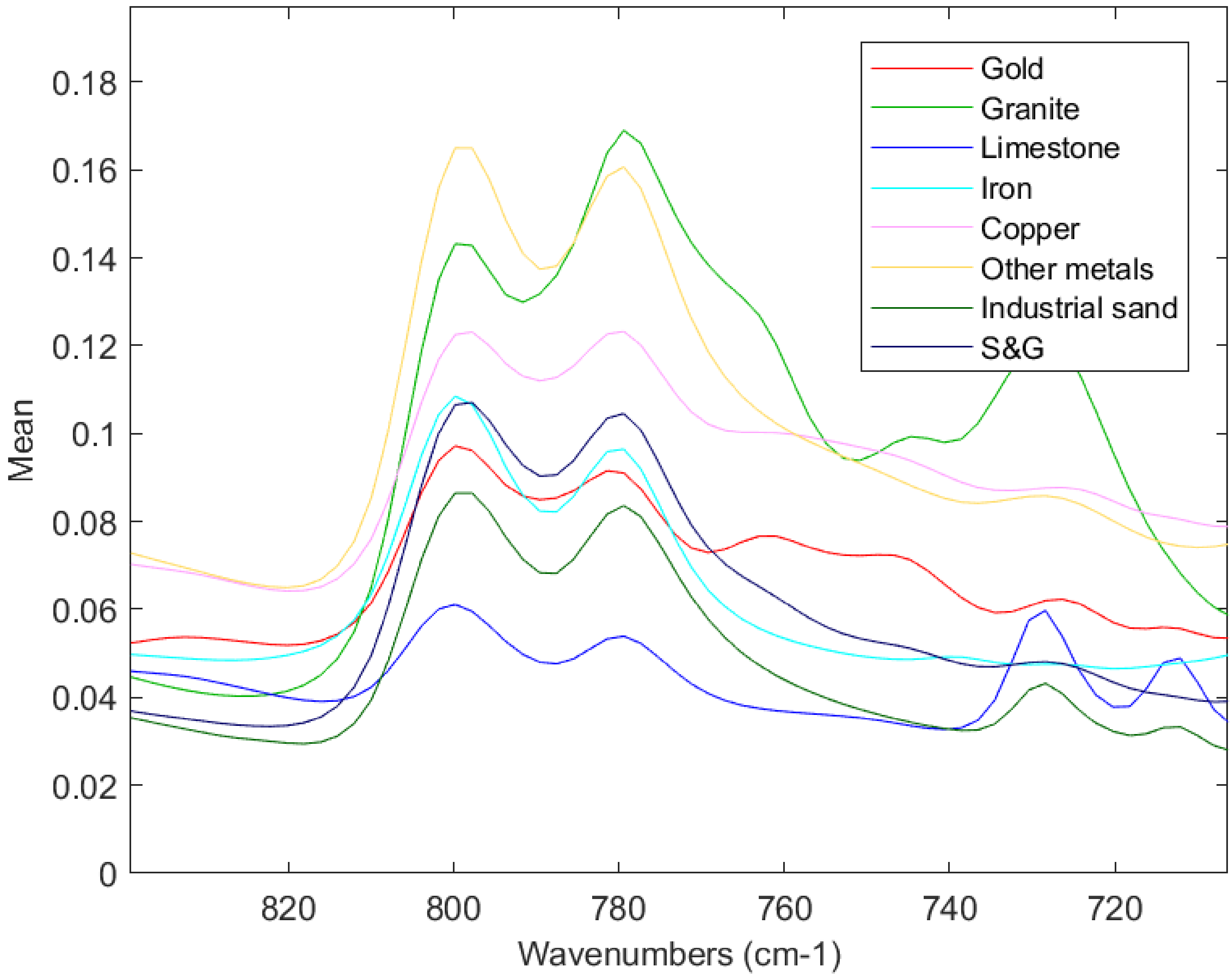

# Principal Components Analysis of FTIR data – Results



# Complexity of mine dusts – FTIR perspective



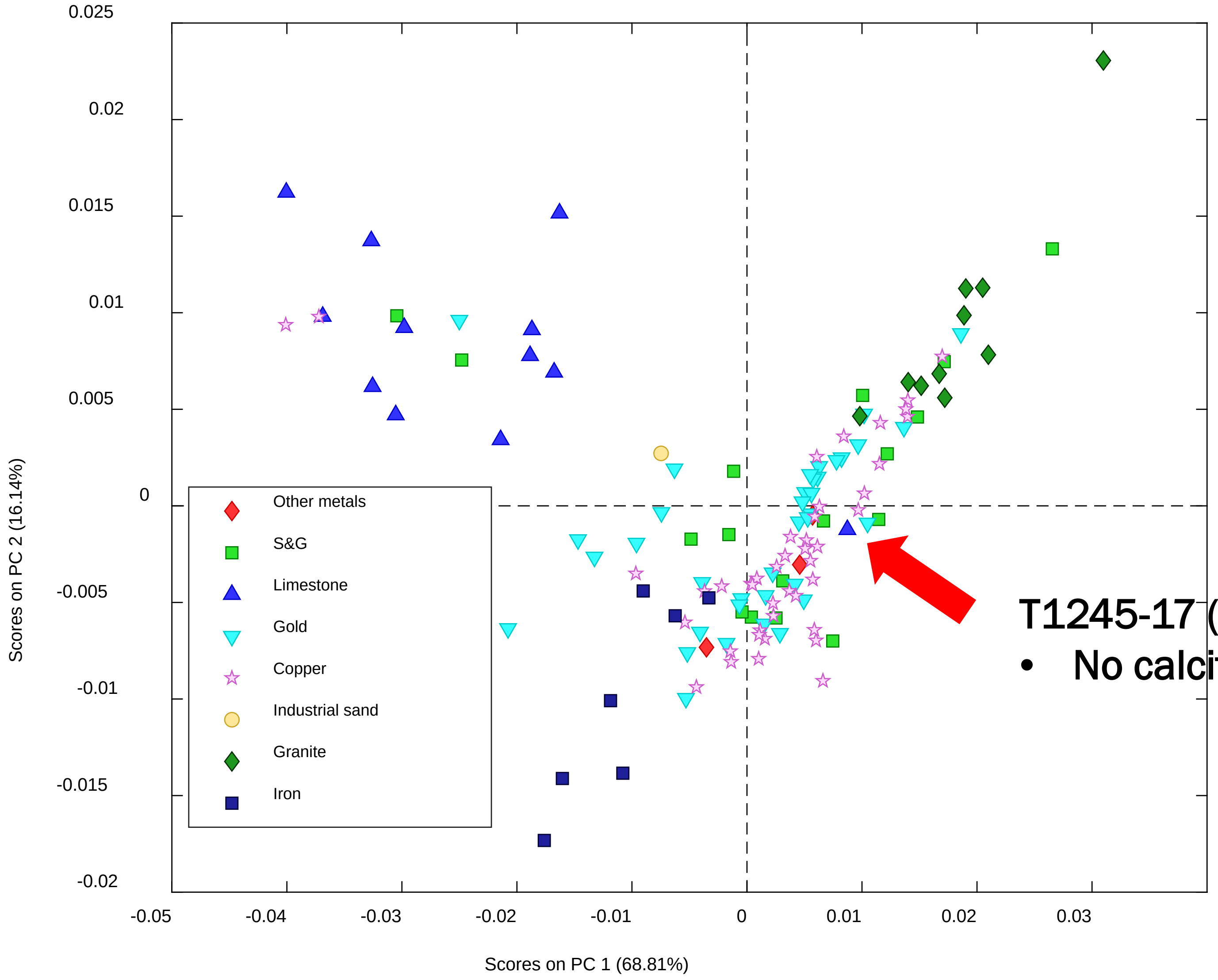

Mean spectra from each type of mining operation




Mean spectral features in silica (quartz) doublet from each type of mining operation

# Principal Components Analysis of FTIR Data

## Scores plots



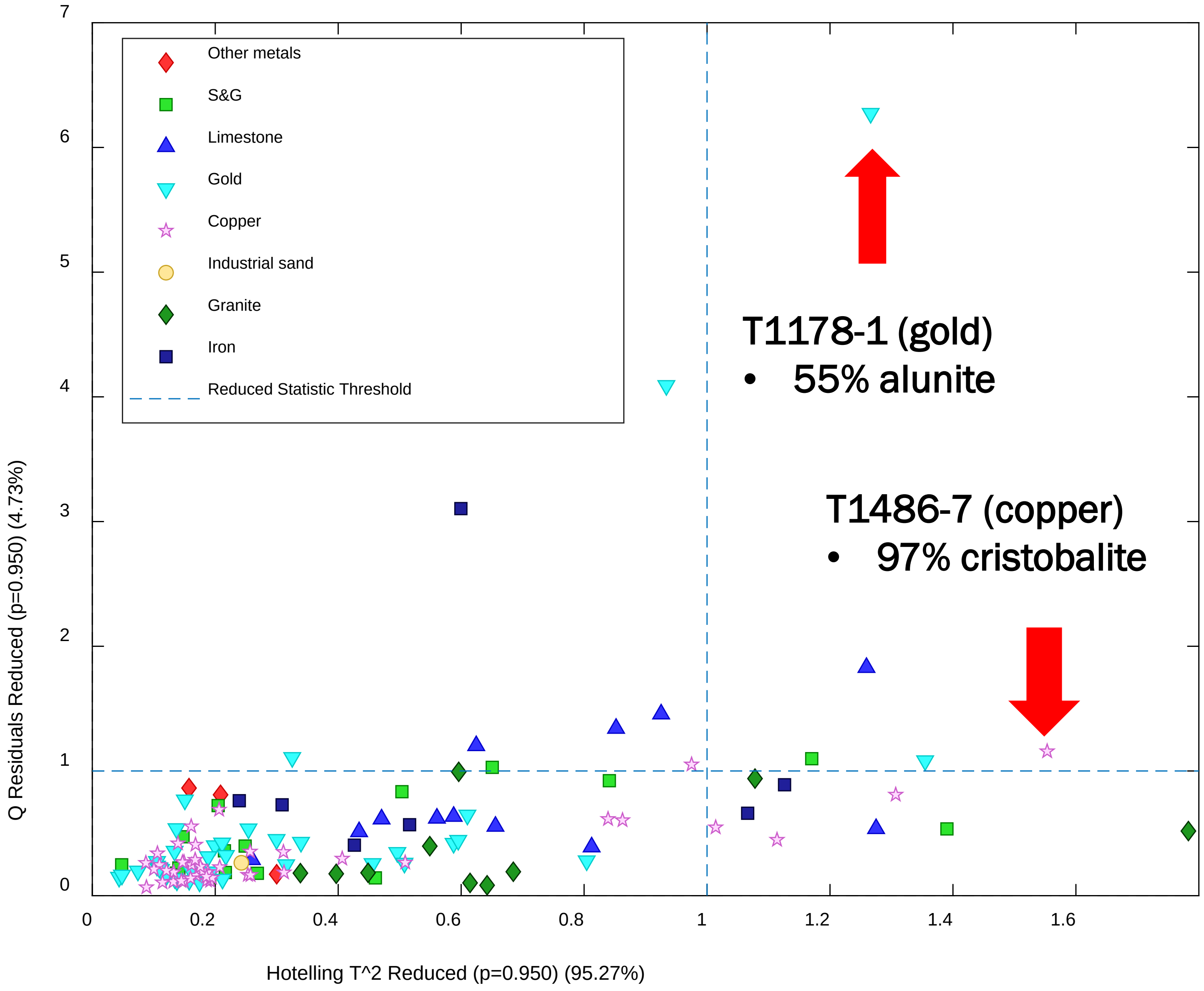

T1245-17 (limestone)

- No calcite or dolomite

Relationships between samples: Limestone and iron samples show strong within-commodity similarities. Differences between copper, gold and S&G samples are less clear.

# Principal Components Analysis of FTIR Data

## Identification of unique samples



# What have we learned?

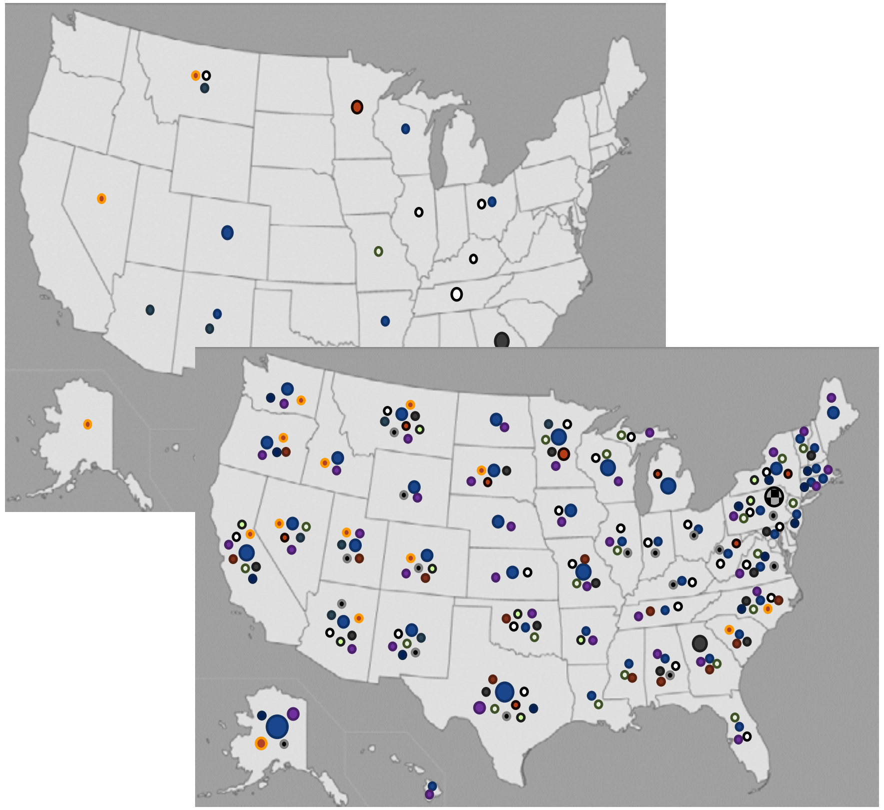
In general

- PCA model can classify limestone samples easily
- Agreement with mineralogy data increases confidence in PCA as an analysis tool
- Iron and granite may be classified with extra effort
- Copper and gold mines are not easily separated from each other

Results of PCA models of XRD and FTIR both show

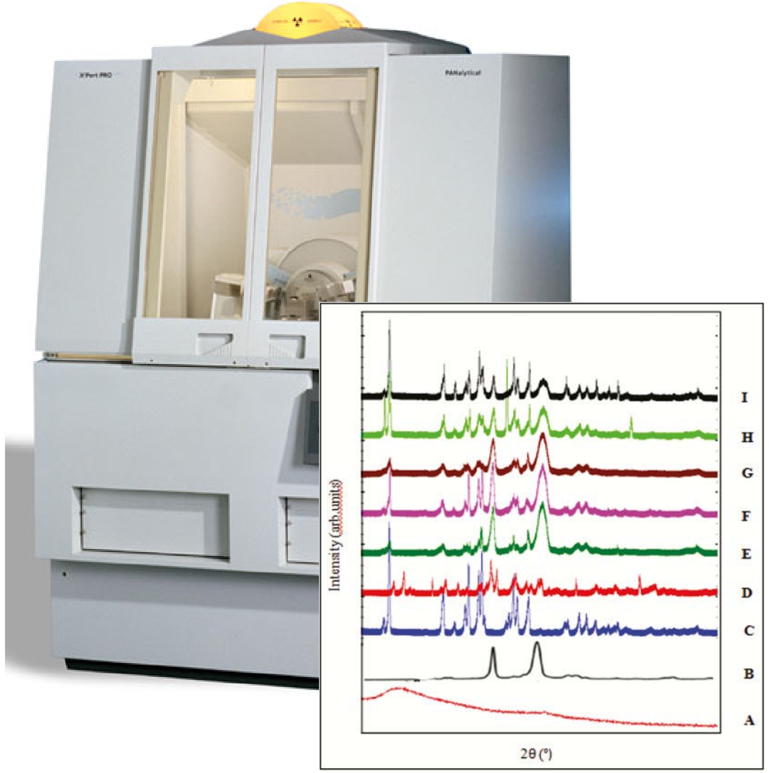
- Identification of samples with unique characteristics
- Some similar patterns and sample groupings
- FTIR may be used for this type of exploratory analysis

# FUTURE WORK



EXPAND NUMBER OF SAMPLES TO IMPROVE MODEL

IMPROVE RESPIRABLE SAMPLING TECHNIQUES




IMPROVE QUALITY OF THE XRD DATA

# Acknowledgements


Audience members

Collaborators
- Robert Stach, Ulm University
- Patrick Krebs, Ulm University
- Cliff Johnston, Purdue University

# EXTRA SLIDES

# Two analytical techniques

## Fourier transform infrared (FTIR) spectroscopy

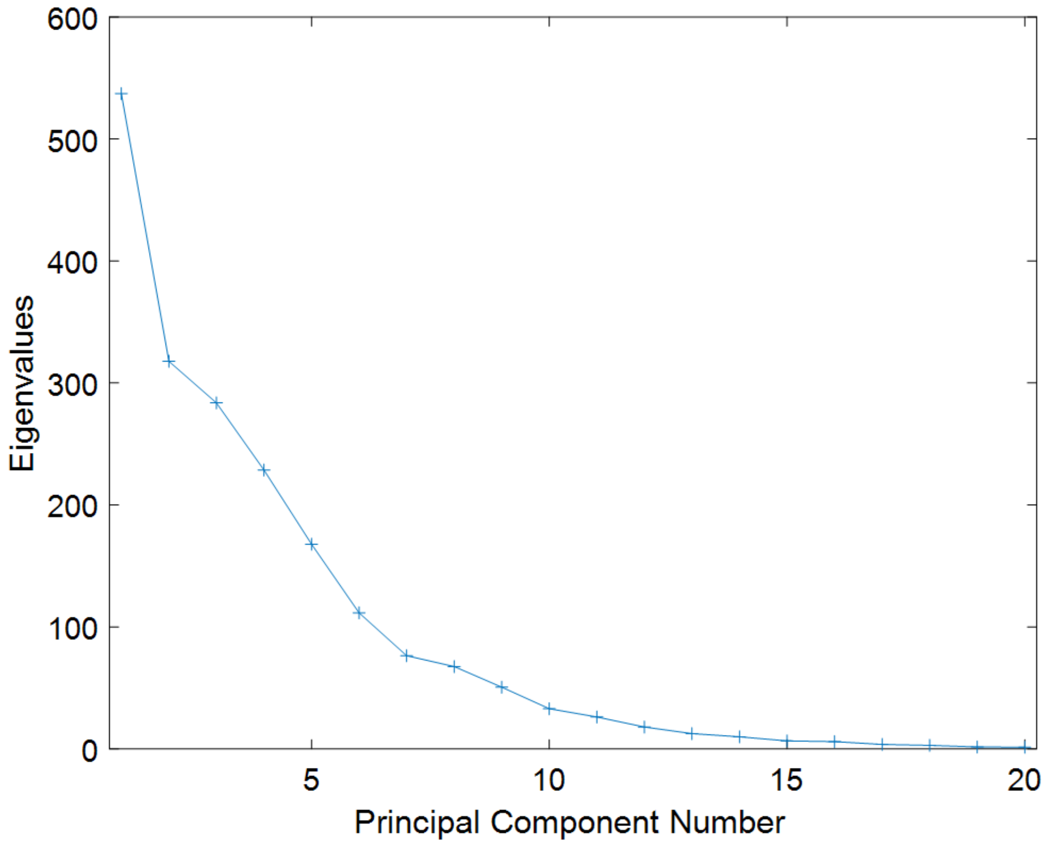
- Bruker alpha
- Analyses performed at NIOSH/PMRD
- Direct-on-filter
- Filter subtracted out

## X-ray powder diffraction (XRD)

- Panalytical X'pert MPD diffractometer, H&M Analytical Services
- Direct-on-filter
- Mineral phase identification with ICSD powder

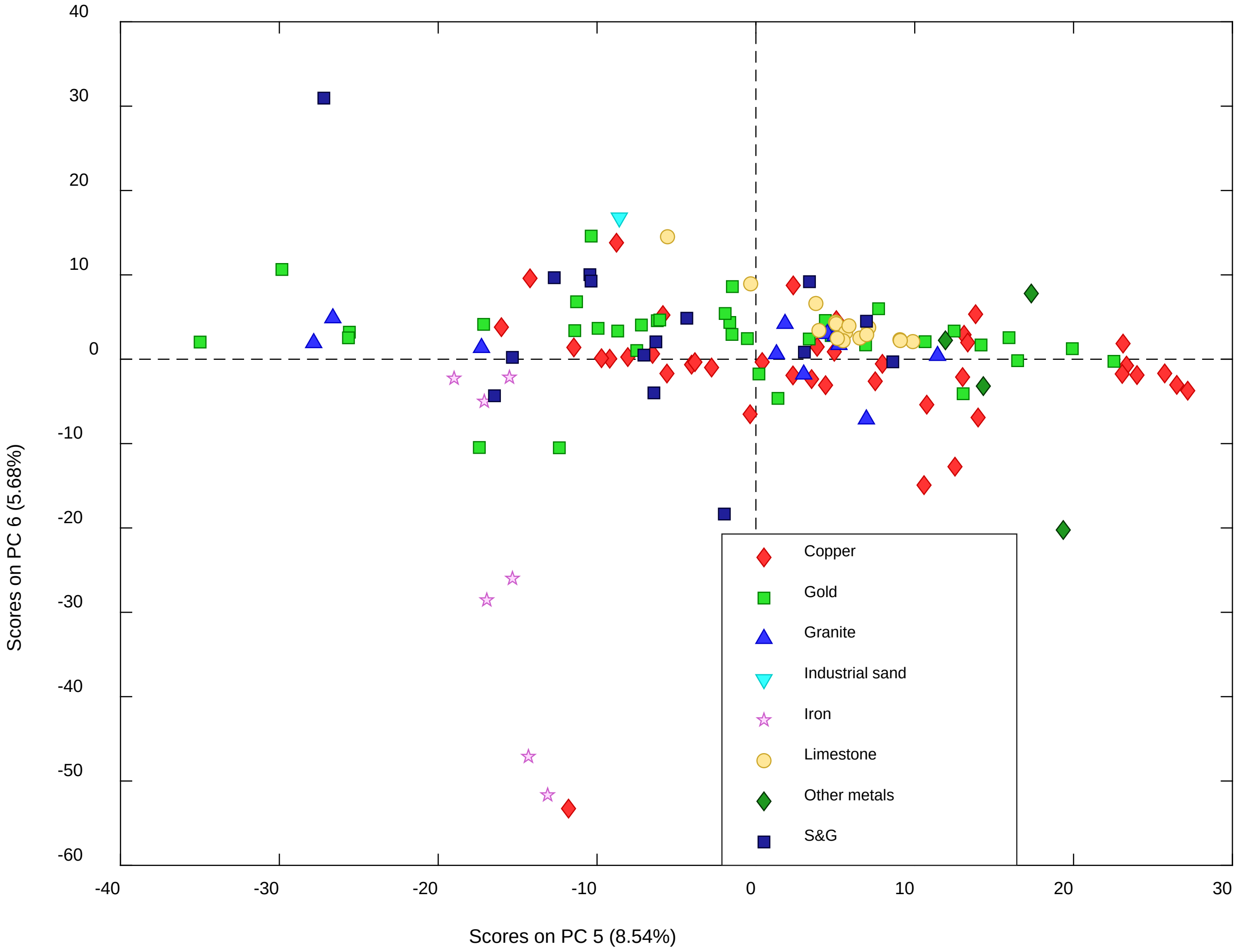
# Estimation of PCA-XRD model – 8 PCs

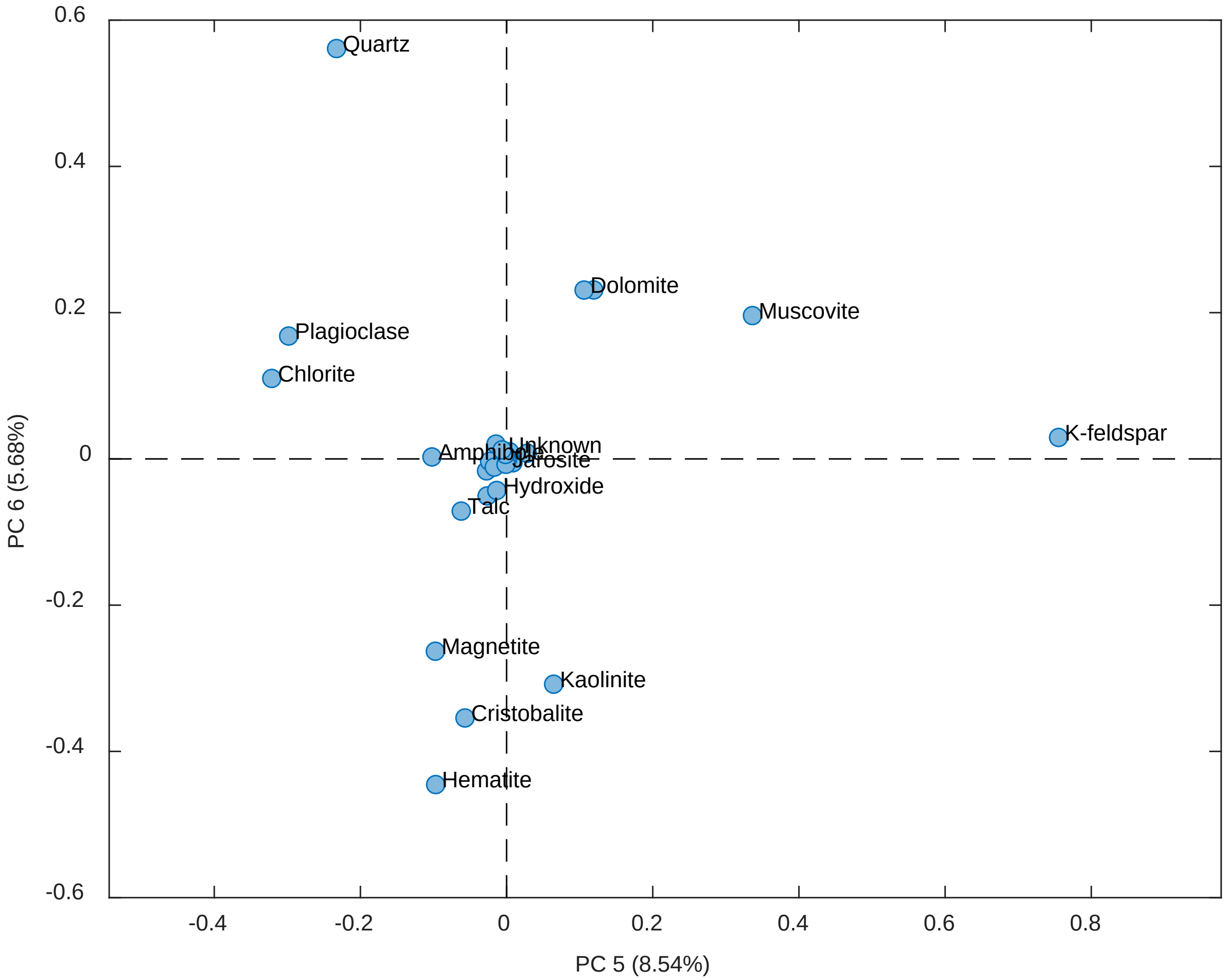
| | Eigenvalue of Cov(X) | % Variance This PC | % Variance Cumulative | RMSEC | RMSECV |
|---|---|---|---|---|---|
| 1 | 5.37e+02 | 27.33 | 27.33 | 6.992 | 8.725 |
| 2 | 3.18e+02 | 16.16 | 43.49 | 6.165 | 9.358 |
| 3 | 2.84e+02 | 14.43 | 57.92 | 5.32 | 12.73 |
| 4 | 2.29e+02 | 11.63 | 69.55 | 4.526 | 14.05 |
| 5 | 1.68e+02 | 8.54 | 78.09 | 3.839 | 13.11 |
| 6 | 1.12e+02 | 5.68 | 83.76 | 3.305 | 16.99 |
| 7 | 7.64e+01 | 3.89 | 87.65 | 2.882 | 21.06 |
| 8 | 6.75e+01 | 3.43 | 91.08 | 2.449 | 27.38 |
| 9 | 5.06e+01 | 2.57 | 93.66 | 2.066 | 26.74 |
| 10 | 3.29e+01 | 1.68 | 95.33 | 1.772 | 42.65 |
| 11 | 2.62e+01 | 1.33 | 96.66 | 1.498 | 63.32 |



# Principal Components Analysis of XRD Data

## Scores and Loadings plots



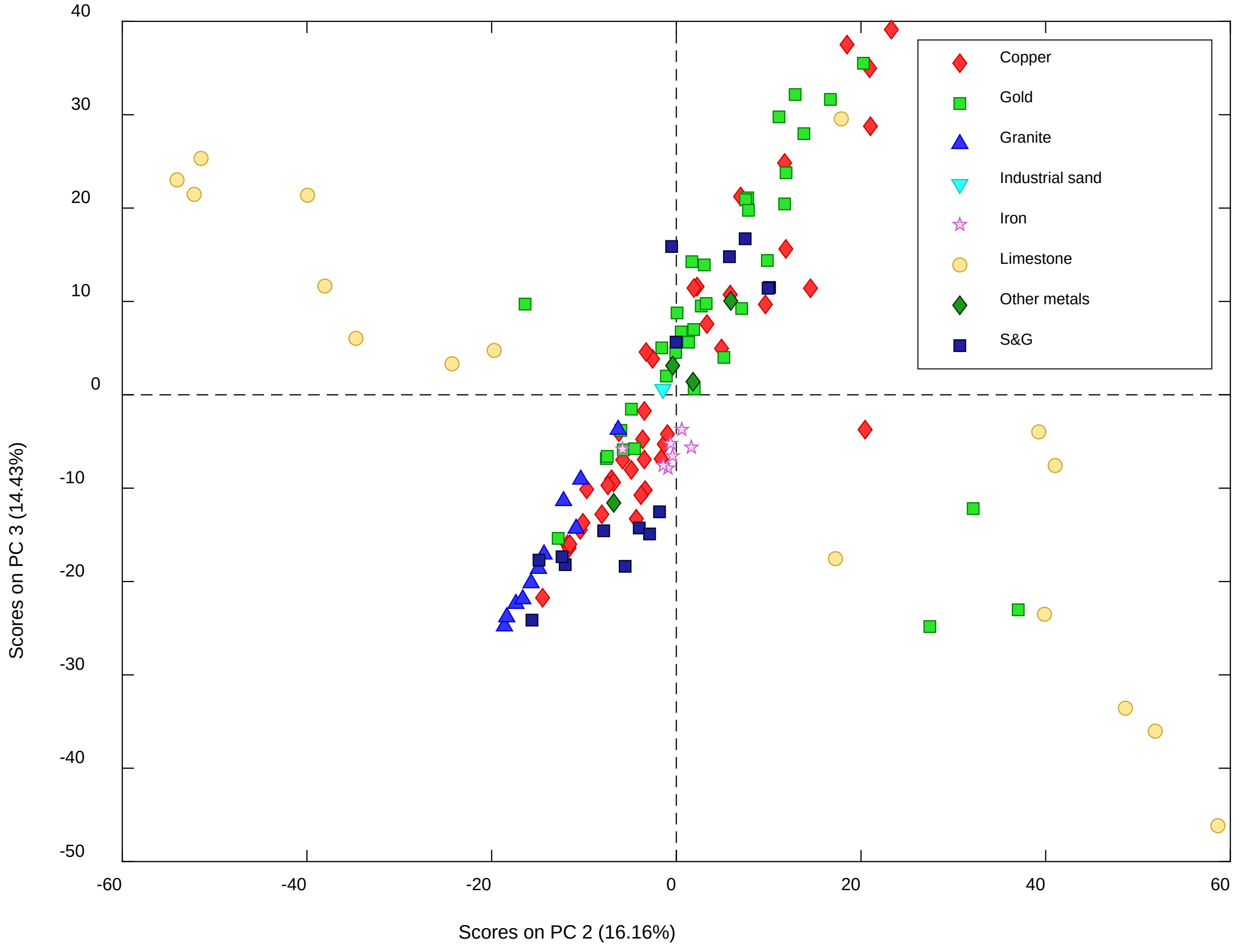



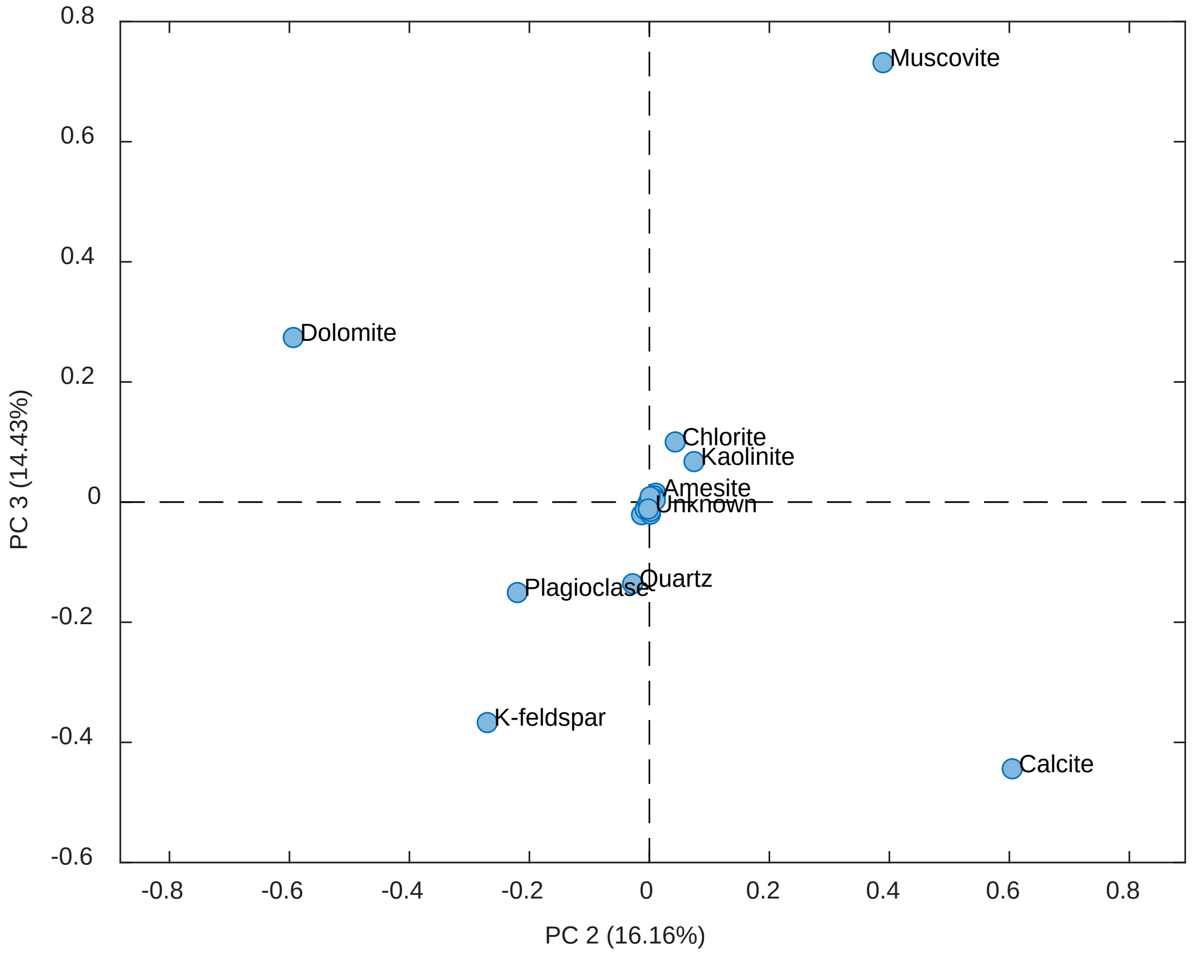

Relationships between samples: iron mine samples show strong variation along PC6

Relationships between variables: quartz, magnetite, hematite strongly influence PC6

# Principal Components Analysis of XRD Data

## Scores and Loadings plots

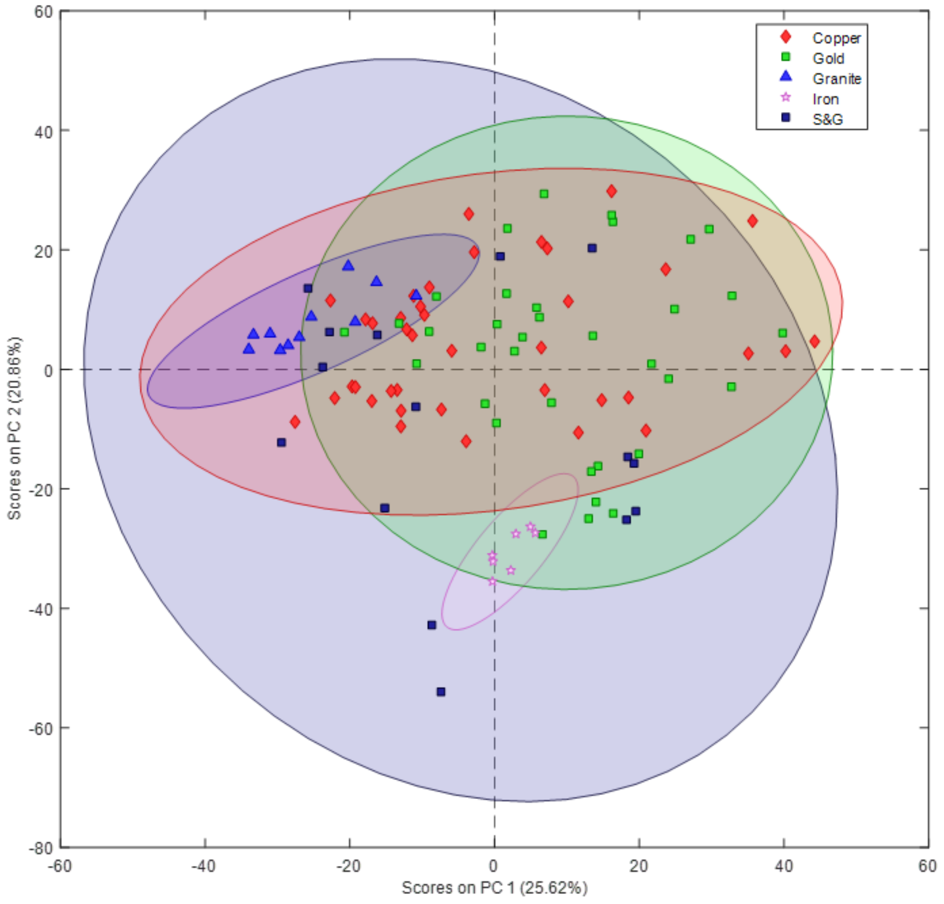


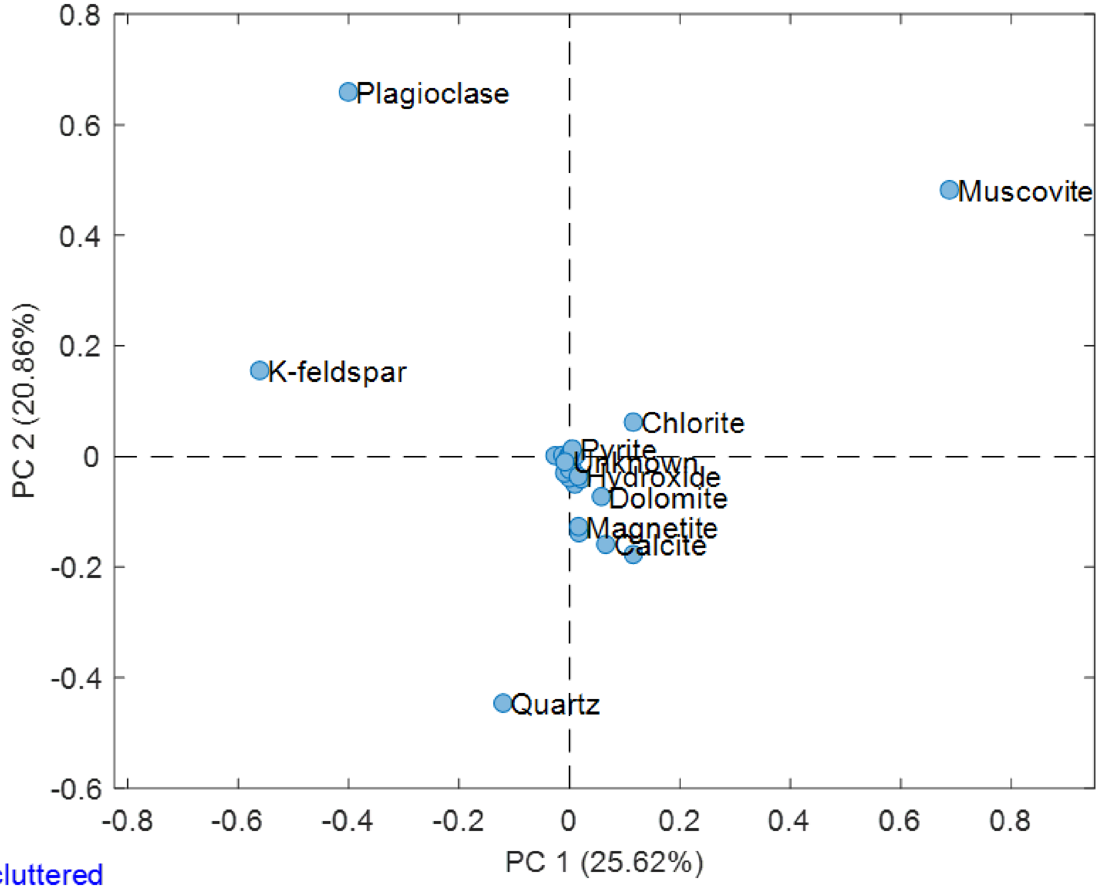




Relationships between samples: limestone mines show strong variation along PC2 and PC3

Relationships between variables: dolomite, calcite and muscovite influence PC2 and PC3

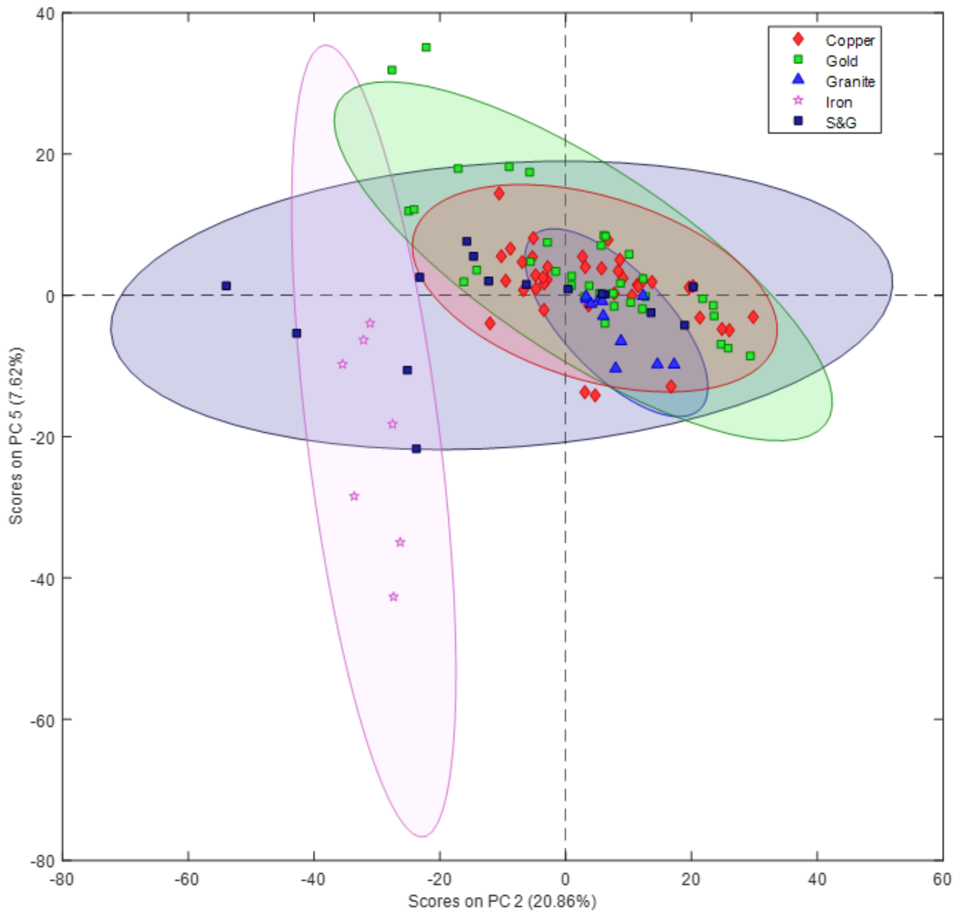
# Removal of limestone mines reveals other structures in the data set

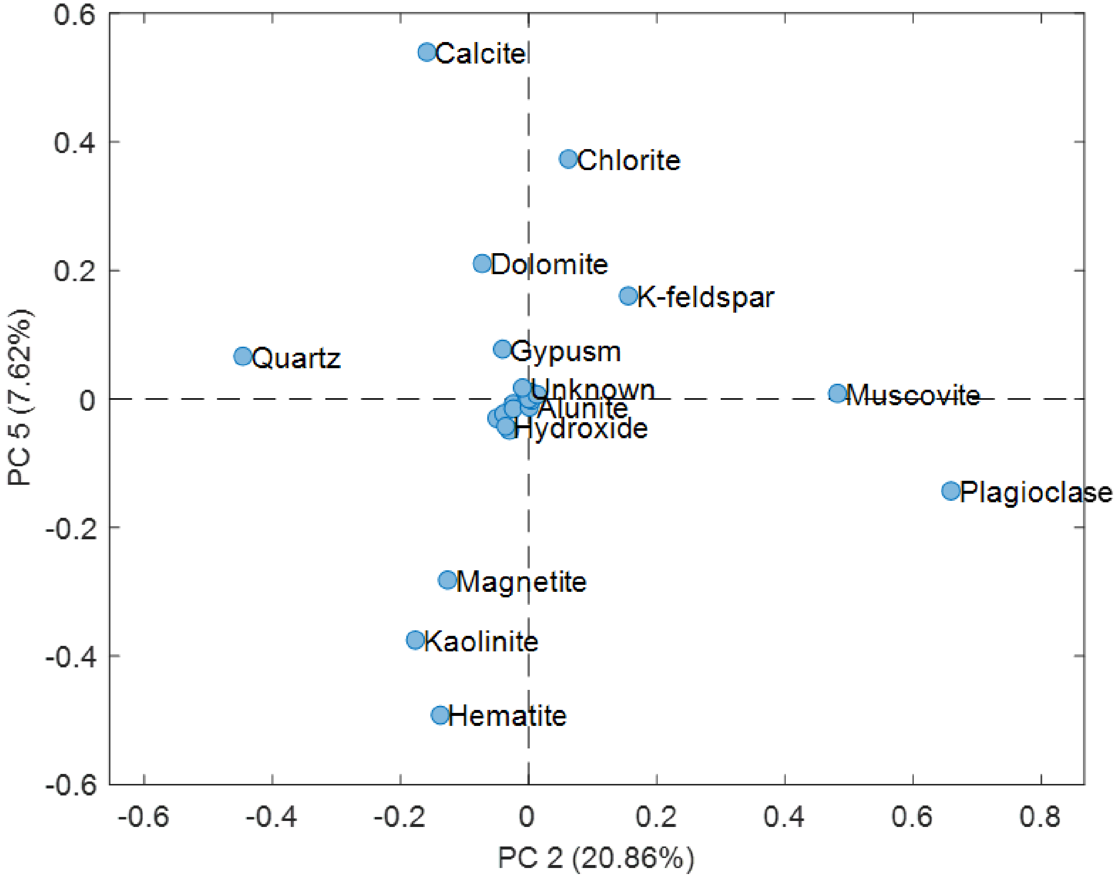


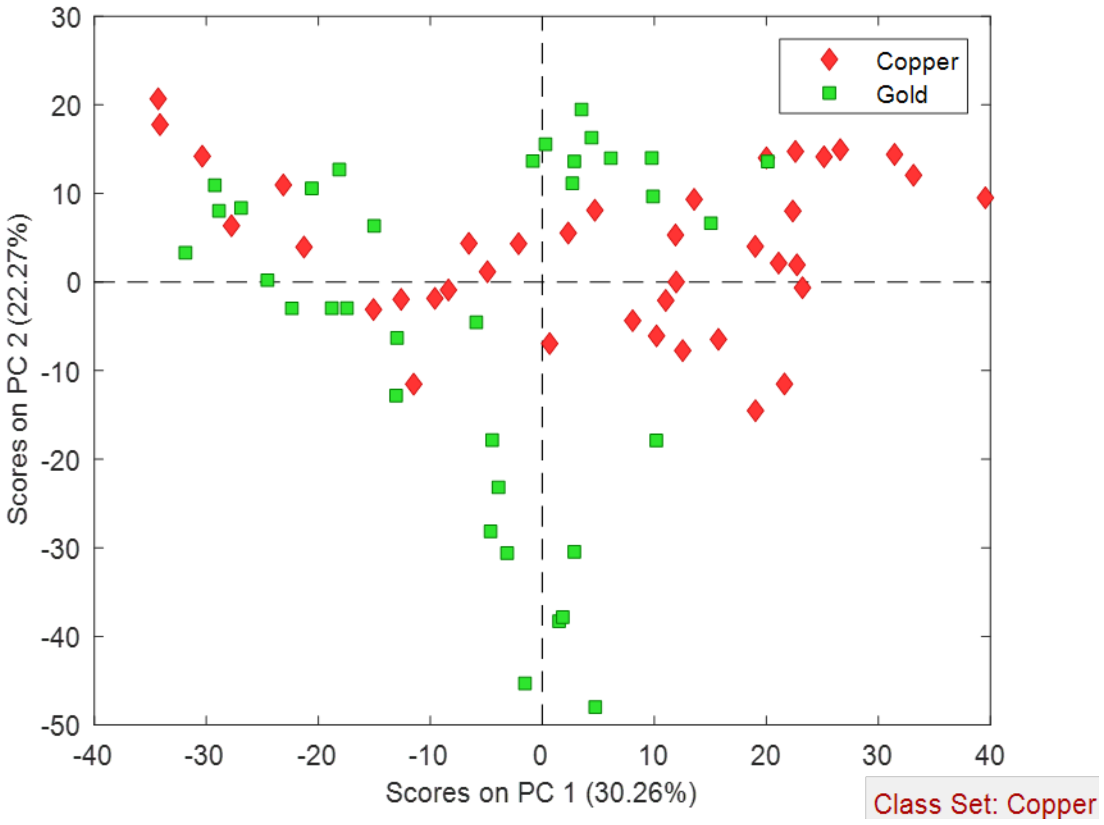

Decluttered

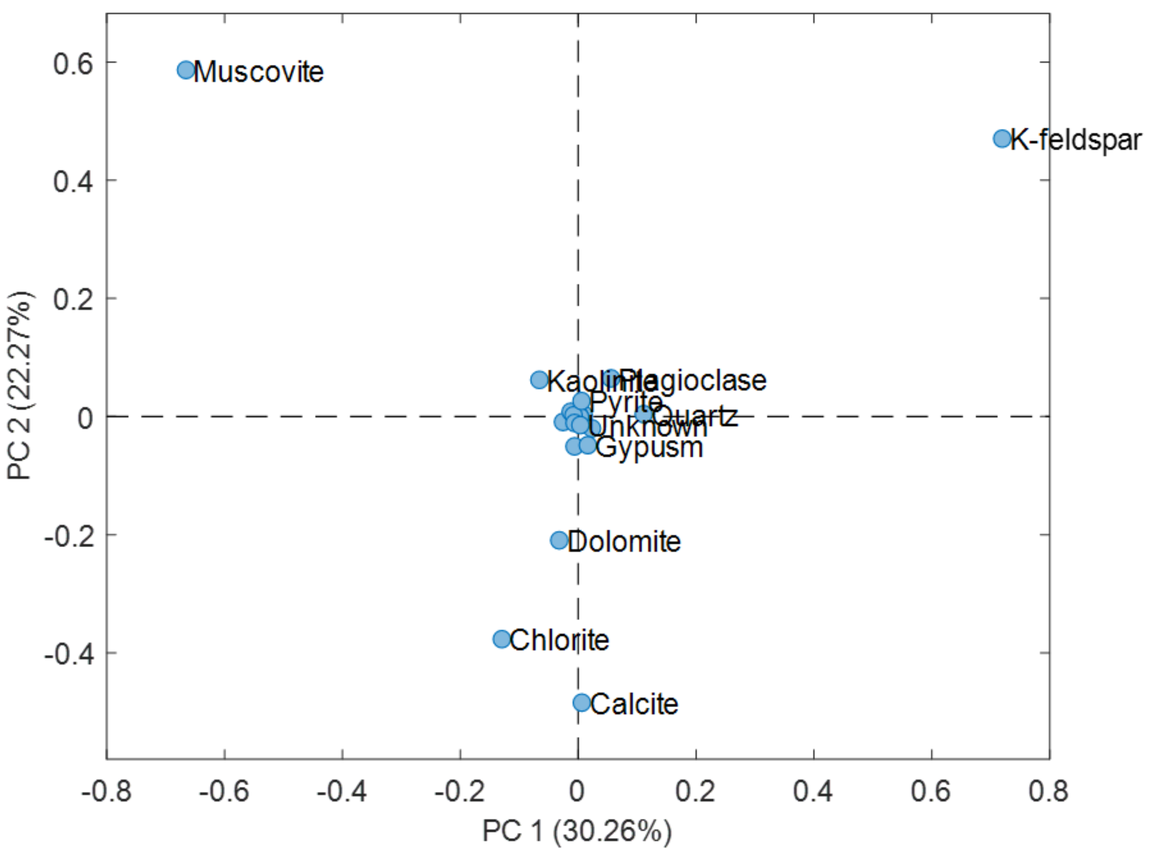
# Removal of limestone mines reveals other structures in the data set



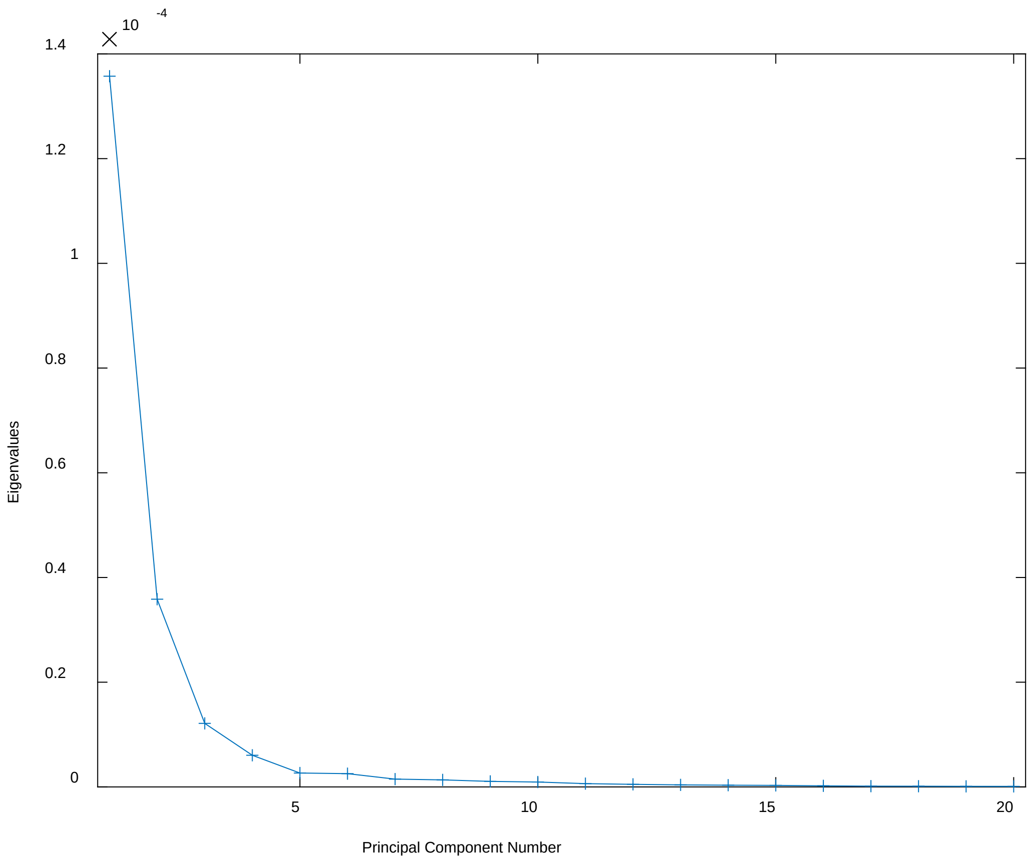
# PCA model of just Gold-Copper



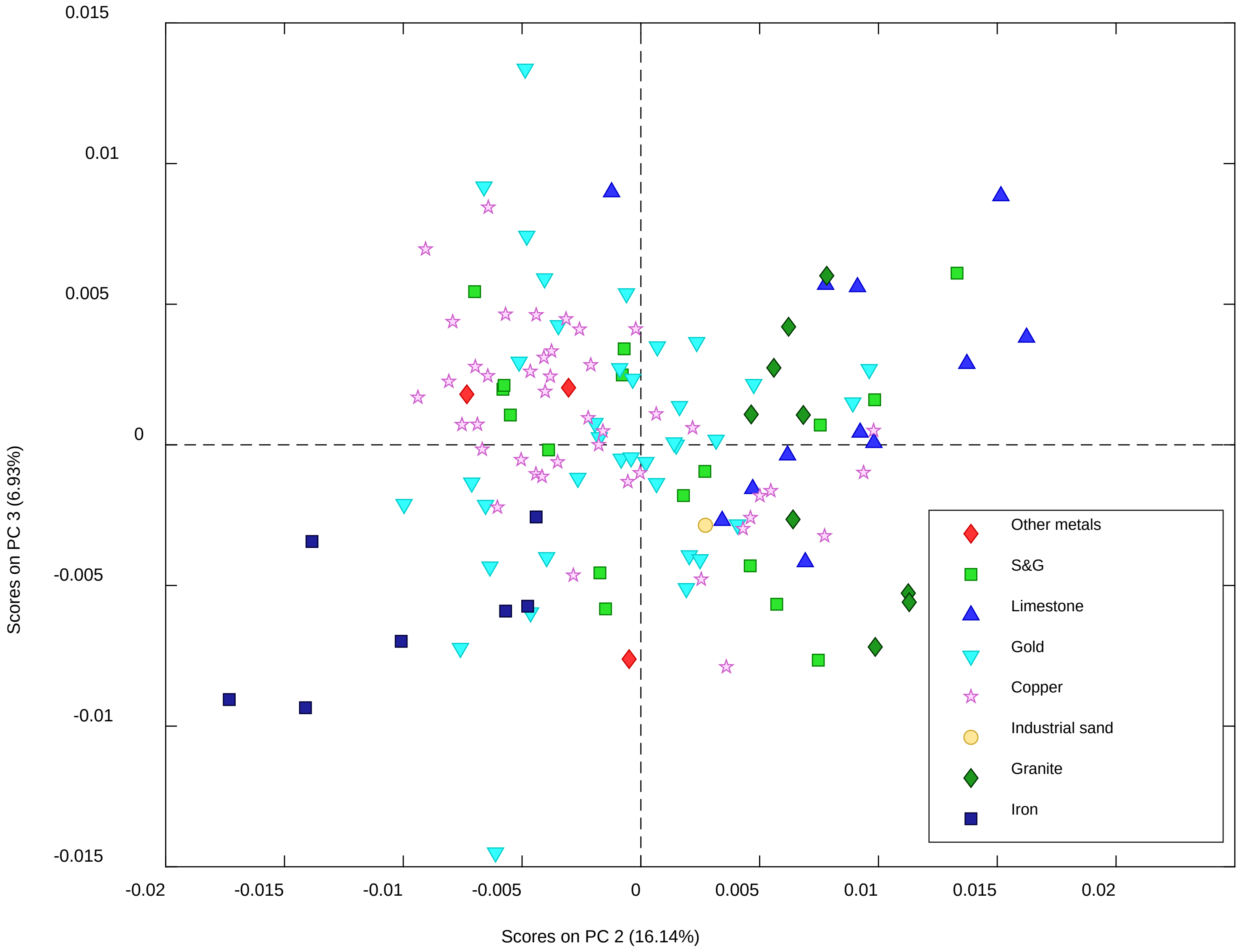
# Estimation of PCA-FTIR model – 5 PCs

| | Eigenvalue of Cov(X) | % Variance This PC | % Variance Cumulative | RMSEC | RMSECV |
|---|---|---|---|---|---|
| 1 | 1.36e-04 | 66.72 | 66.72 | 0.0001951 | 0.0002288 |
| 2 | 3.59e-05 | 17.62 | 84.34 | 0.0001338 | 0.0001535 |
| 3 | 1.21e-05 | 5.97 | 90.31 | 0.0001053 | 0.0001288 |
| 4 | 6.04e-06 | 2.97 | 93.28 | 8.768e-05 | 0.0001135 |
| 5 | 2.65e-06 | 1.30 | 94.58 | 7.871e-05 | 0.000114 |
| 6 | 2.53e-06 | 1.24 | 95.83 | 6.908e-05 | 0.0001056 |
| 7 | 1.49e-06 | 0.73 | 96.56 | 6.272e-05 | 0.0001075 |
| 8 | 1.34e-06 | 0.66 | 97.22 | 5.639e-05 | 0.0001014 |
| 9 | 1.06e-06 | 0.52 | 97.74 | 5.085e-05 | 0.0001043 |
| 10 | 9.33e-07 | 0.46 | 98.20 | 4.54e-05 | 0.0001027 |
| 11 | 6.28e-07 | 0.31 | 98.51 | 4.133e-05 | 0.0001019 |
| 12 | 4.93e-07 | 0.24 | 98.75 | 3.783e-05 | 0.0001013 |



# Principal Components Analysis of FTIR Data

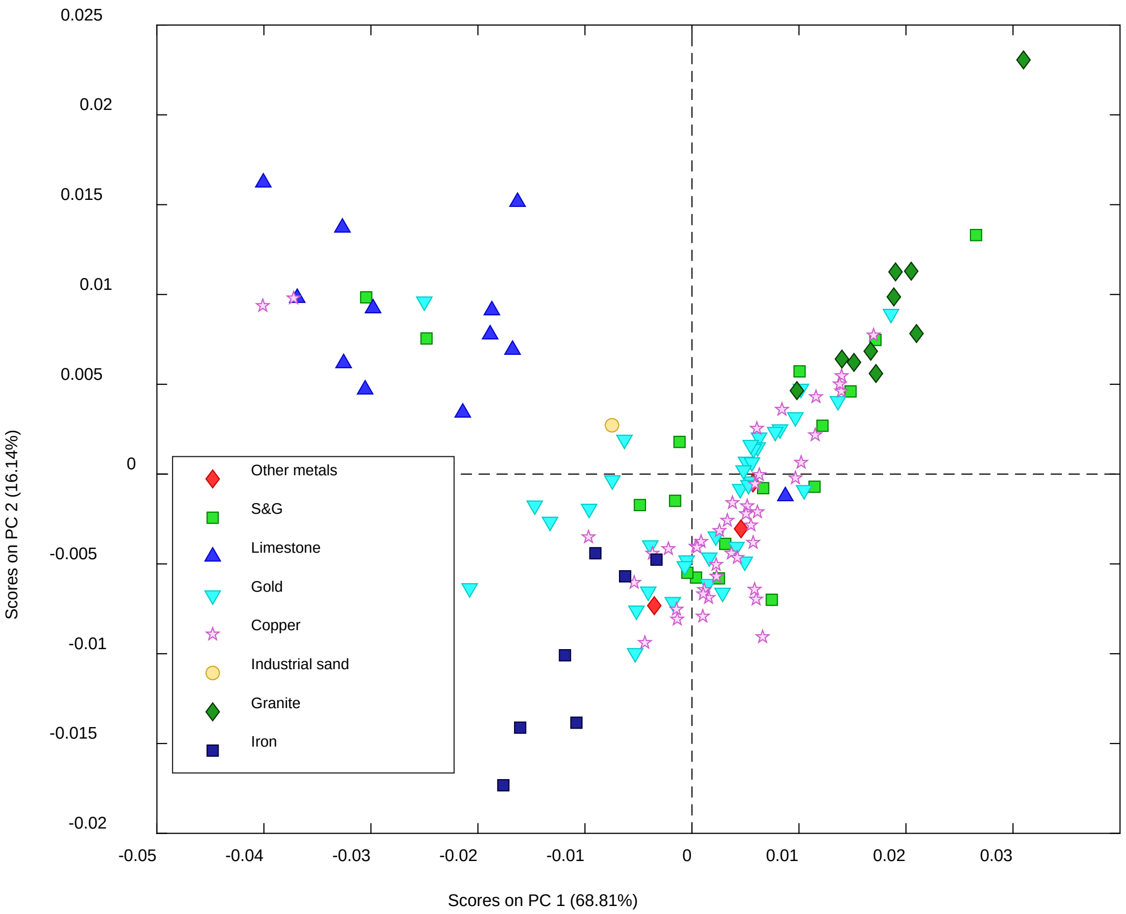
## Scores plots

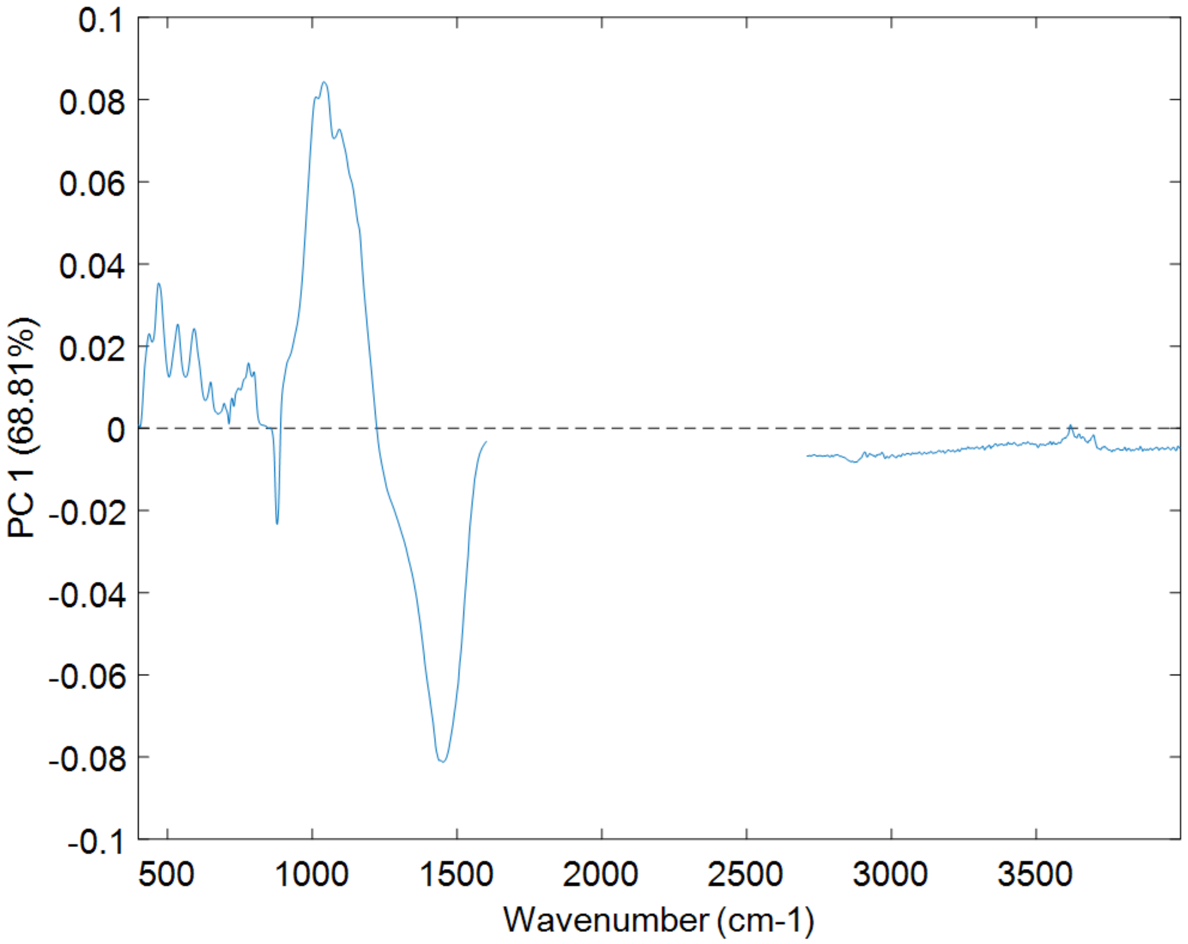



Relationships between samples: limestone samples spread more across PC3 and PC2 and are harder to distinguish from other sample types.

# Principal Components Analysis of FTIR Data

## Scores and loadings Plots



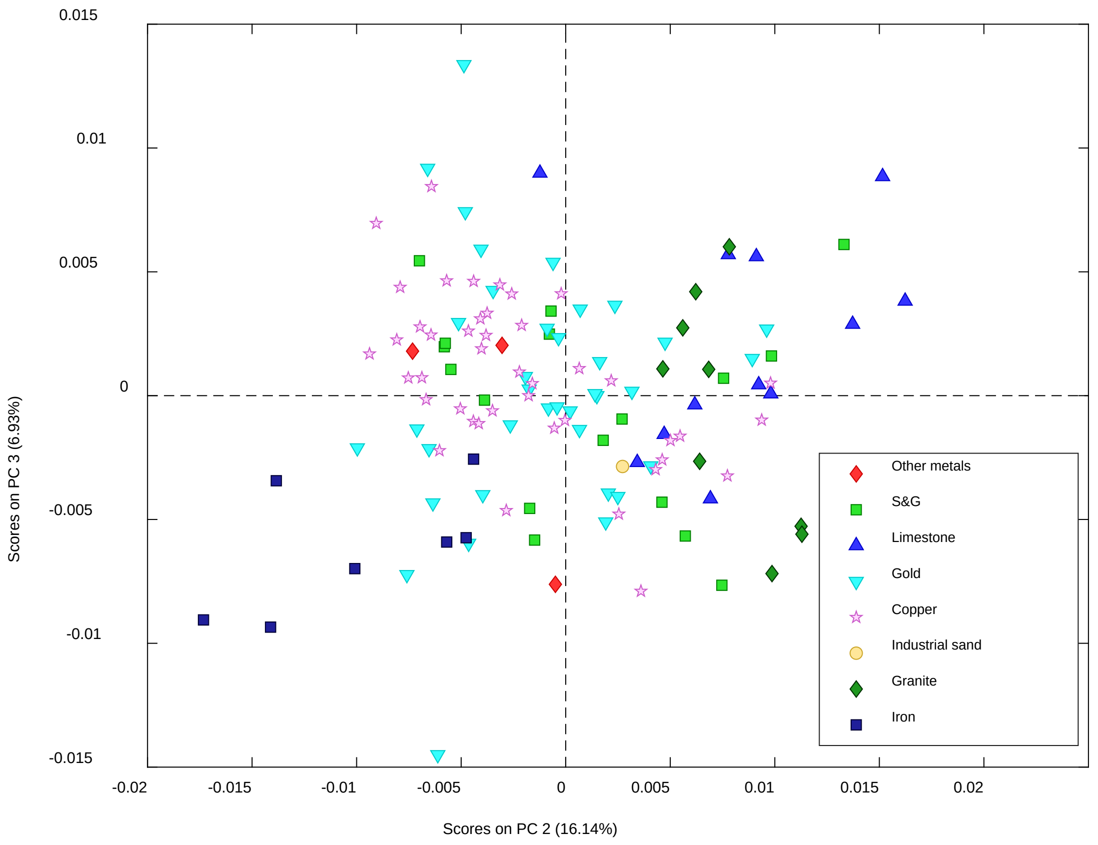



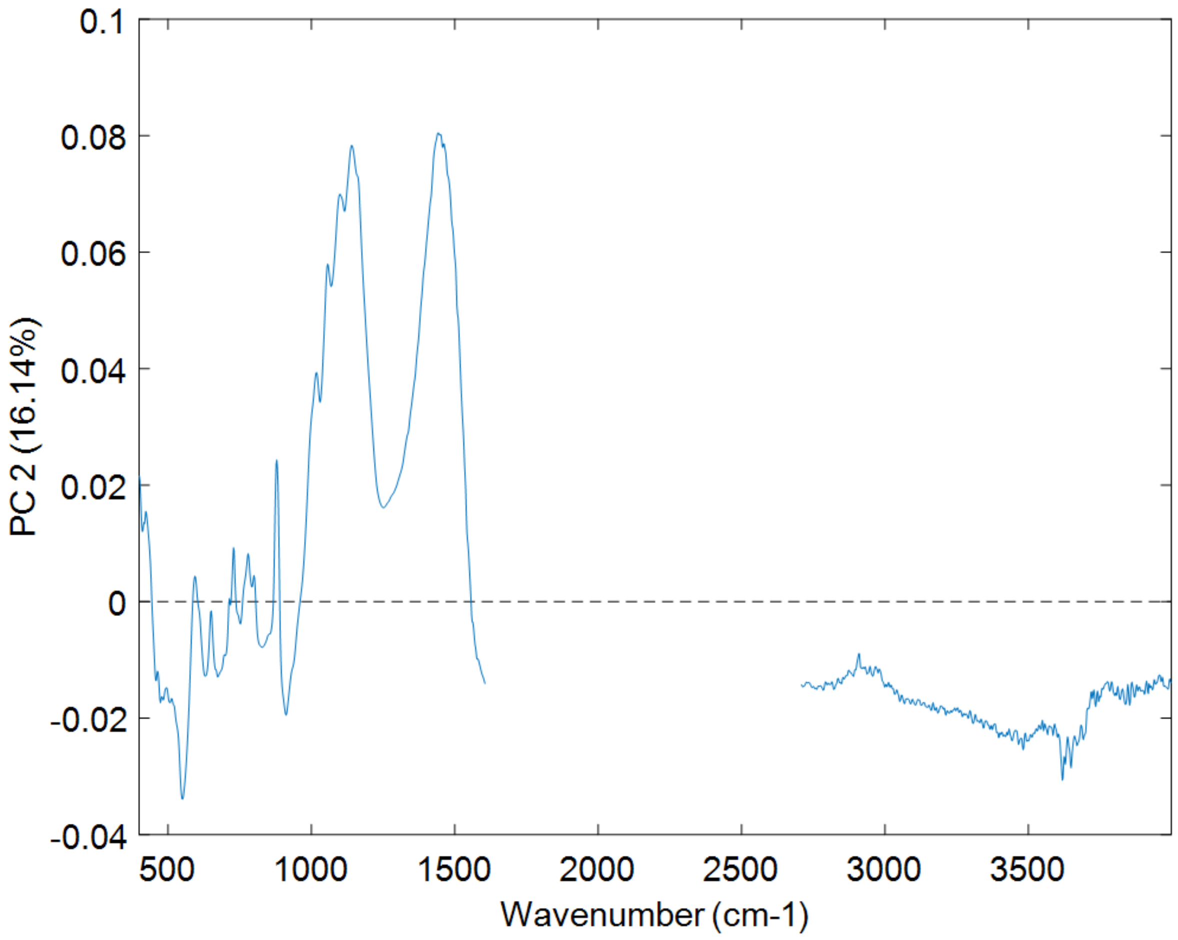

Relationships between samples:

Relationships between variables:

# Principal Components Analysis of FTIR Data

## Scores and loadings Plots




Relationships between samples:

Relationships between variables: