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# MULTIVARIATE STATISTICAL ANALYSIS of MICRO-XRF SPECTRAL IMAGES FROM A BRUKER M4 TORNADO SYSTEM

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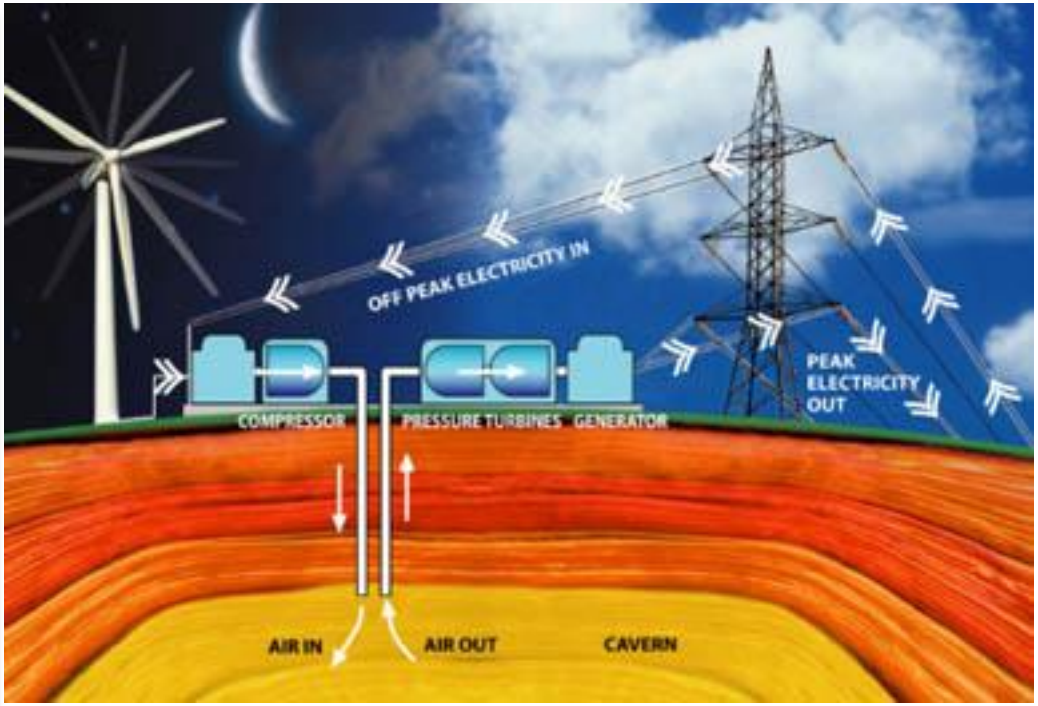
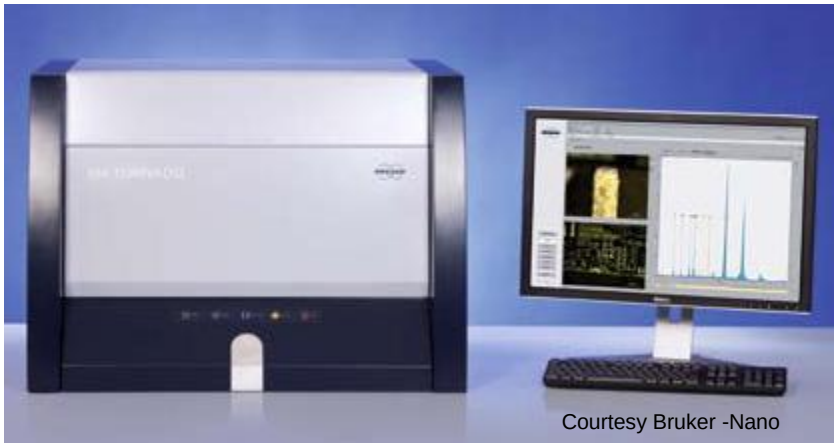
# Compressed Air Energy Storage (CAES) is important for renewable (Wind) energy systems

- CAES requires comprehensive characterization of the underground geological formation
- Reaction of Pyrite with injected air is of significant concern
- XRD and XRF analysis were used to analyze core-drilled samples
- Principle Component Analysis (PCA) was used to decompose convoluted μ-XRF datasets
- XRF results were used to improve trace phase identification of the quantitative XRD results




www.reuk.co.uk/Storing-Wind-Power-with-Compressed-Air.htm



Courtesy Bruker -Nano

## Bruker M4 Tornado μ-XRF

- Rh microfocus source 50 kV/ 600 μA
- High flux polycapillary optic
- ~30 μm spatial resolution
- XFlash® silicon drift detector

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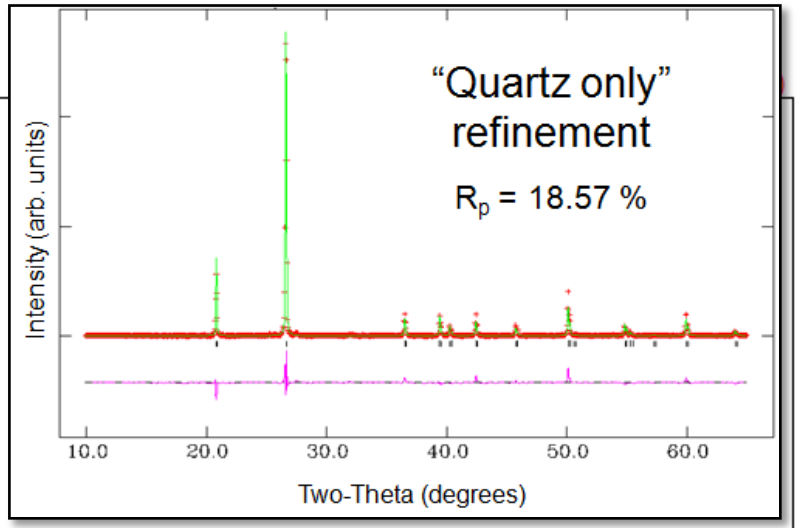
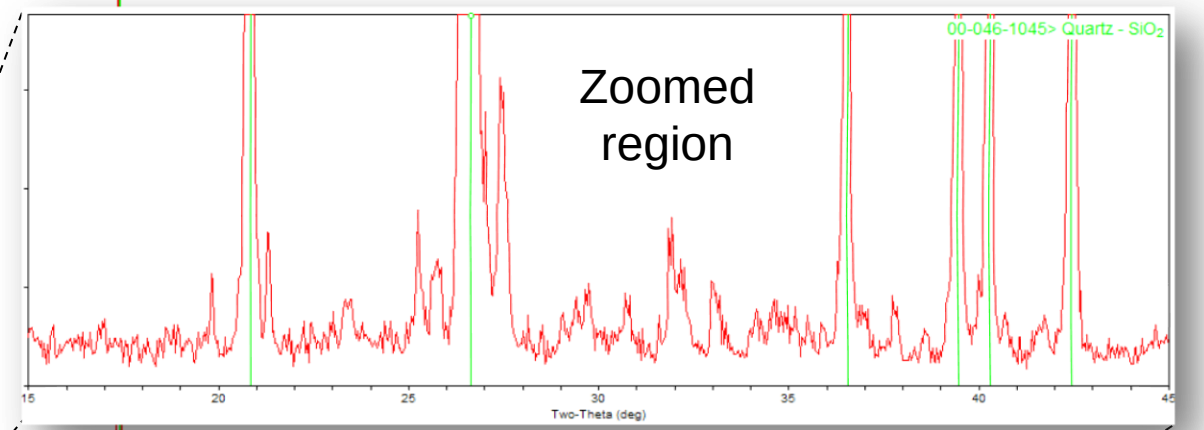
# XRD Result

## First glance: Quartz

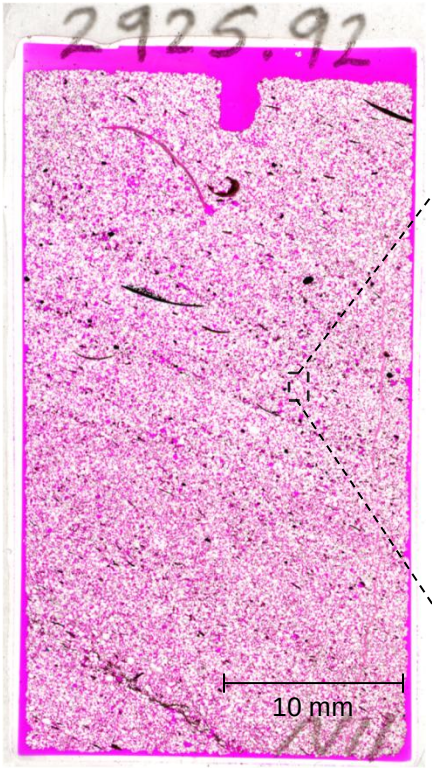
…but zoom shows trace phases.

- Specimen run as a ground powder (< 20 μm)
- Conventional θ-2θ PXRD
  - Siemens D500
  - Cu Kα, graphite monochromator

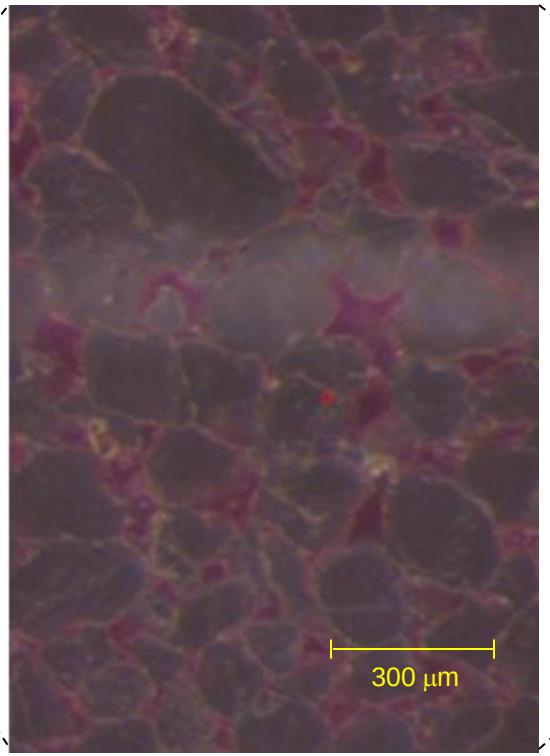


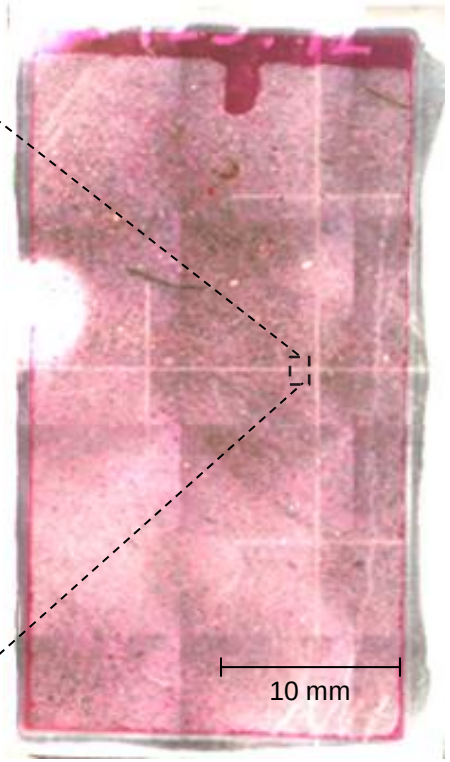
Core-drilled material was prepared as a thin-section (~30 μm thickness). The pink appearance is from an epoxy-resin stain employed to enhance the pore space. Optical microscopy imaging on the prepared core cross-section as shown was performed within the M4 μ-XRF chamber via the video microscope.




Thin-section scan of core sample from primary flow unit

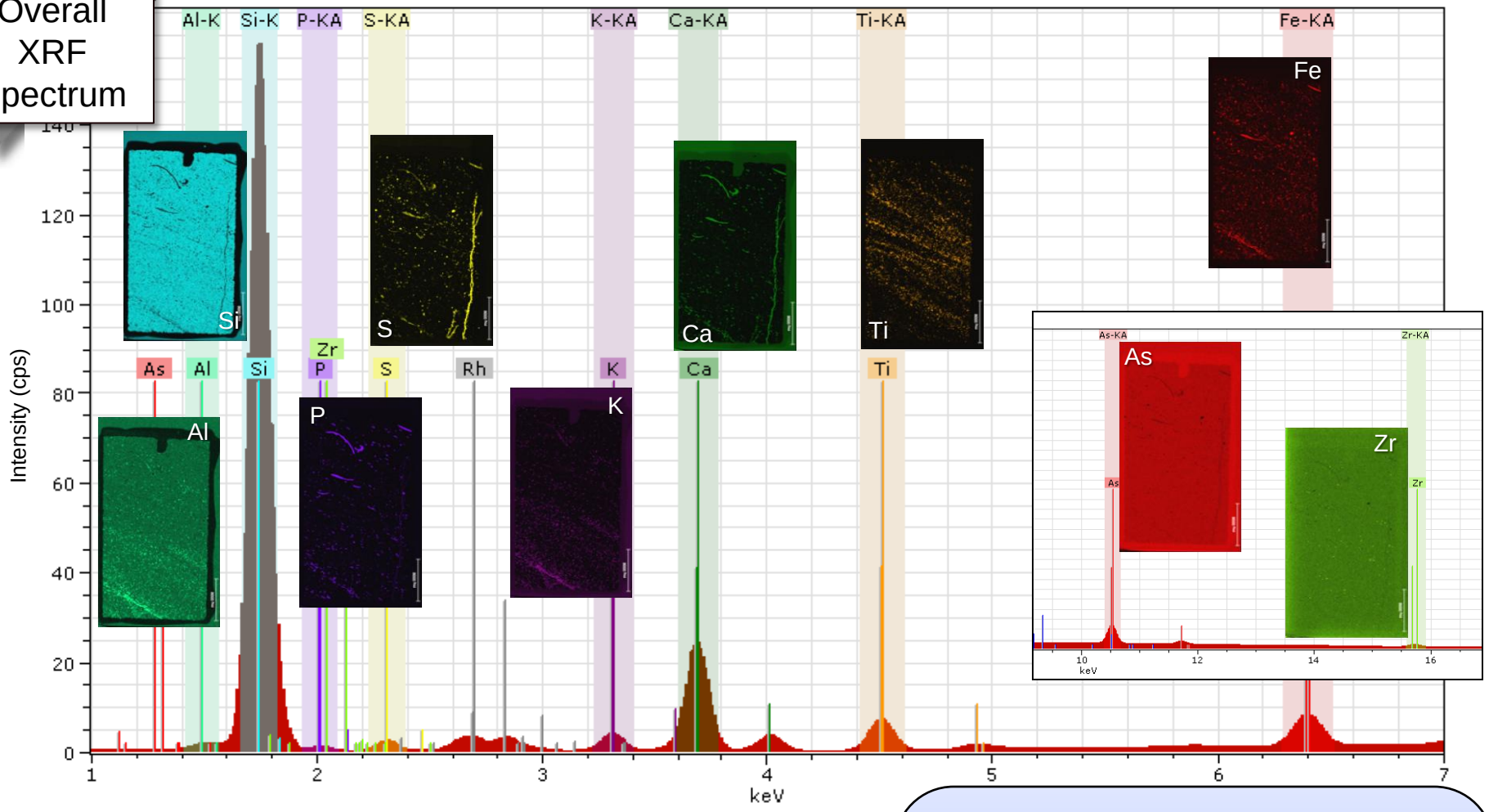



Zoomed video image from M4 showing large Quartz grains (pink color indicates connected porosity)

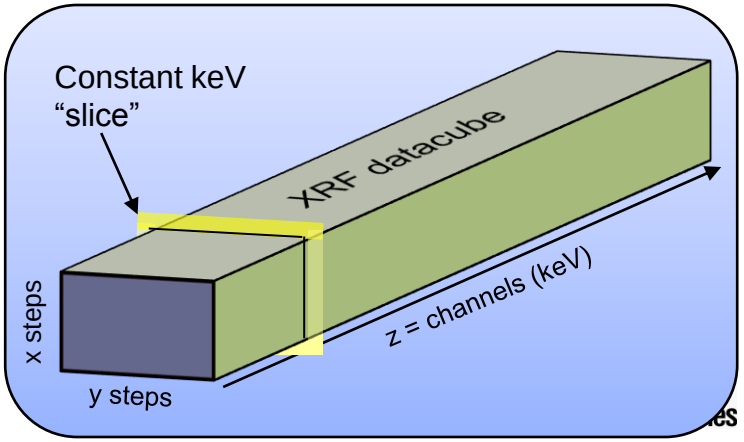



Mosaic video image of cross-section from M4 μ–XRF

# Overall XRF Spectrum




Conventional elemental mapping plots the x-y spatial map at a fixed keV range of the dataset (i.e. a “slice” of the datacube). Here are shown the overall XRF spectrum and the associated elemental slice maps for the core-drilled sample.

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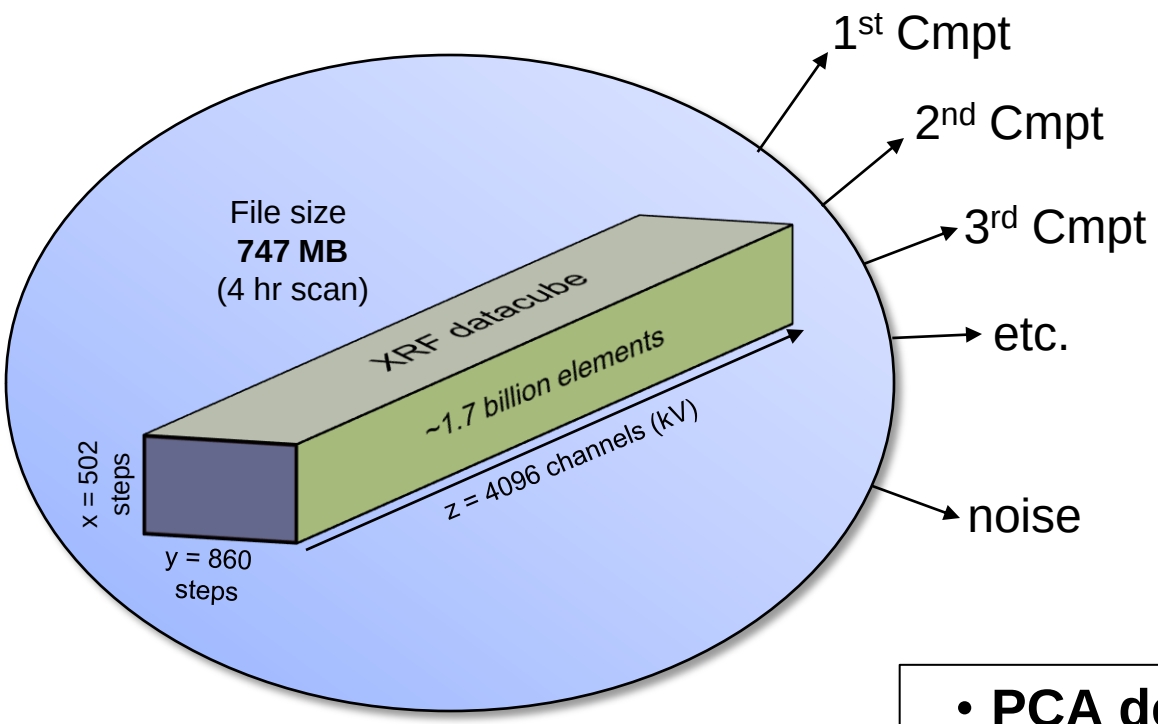
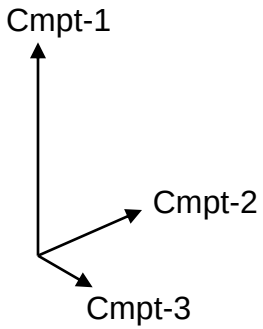
A form of Multivariate Analysis called Principal Component Analysis **(PCA)** can be used to reduce ***massive*** datasets such as those from the M4 μ-XRF




Each derived **component** is mathematically constrained to be orthogonal to others

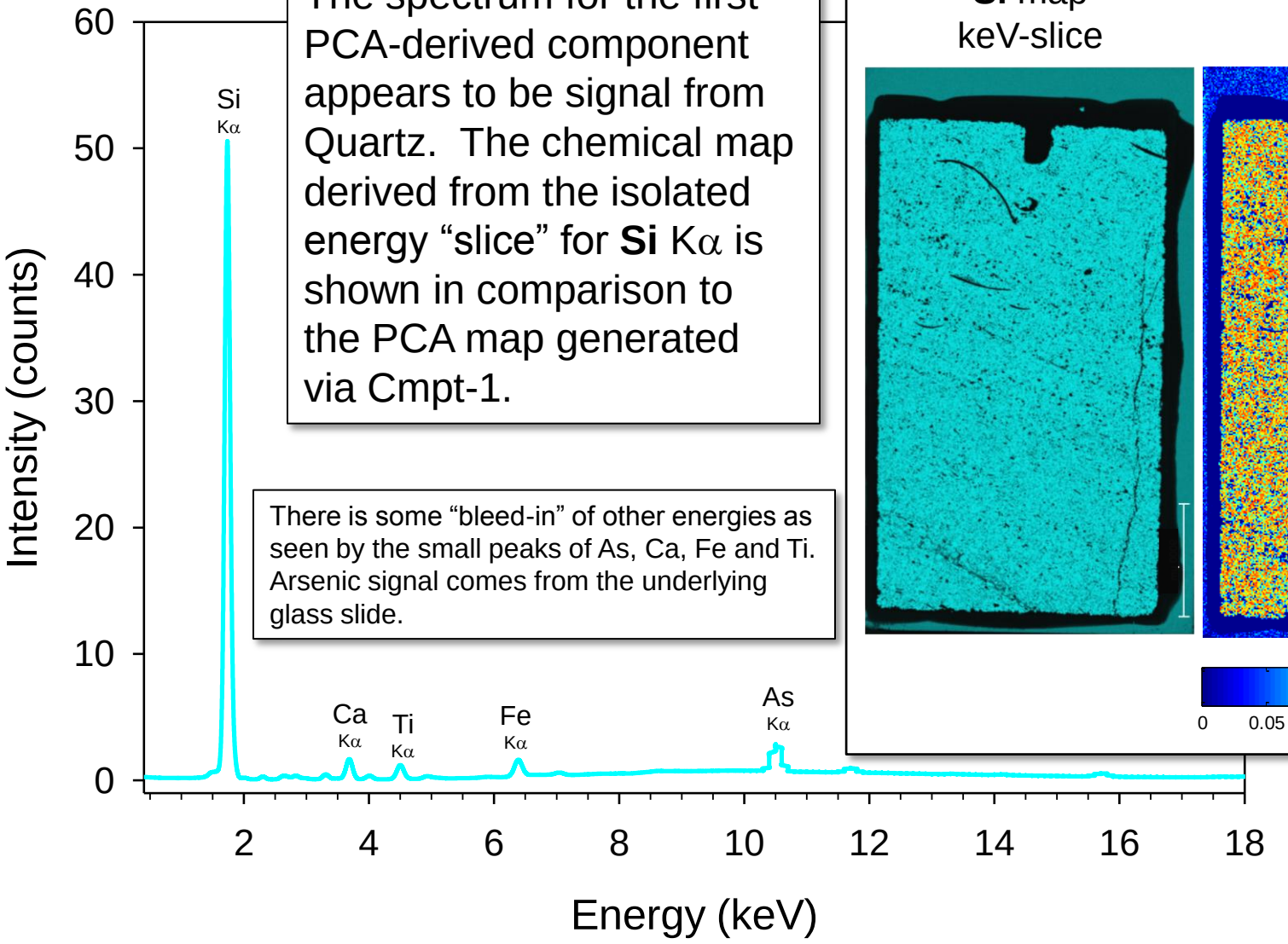
We assume that the entire XRF datacube can be represented by ***linear combinations*** of all species generating fluorescence signal

- **PCA decomposes XRF spectra using the entire datacube to find energy features common to given spatial locations**
- **This approach is much more effective for compositional ID**

# Component 1 Quartz

The spectrum for the first PCA-derived component appears to be signal from Quartz. The chemical map derived from the isolated energy "slice" for **Si** Kα is shown in comparison to the PCA map generated via Cmpt-1.

There is some "bleed-in" of other energies as seen by the small peaks of As, Ca, Fe and Ti. Arsenic signal comes from the underlying glass slide.







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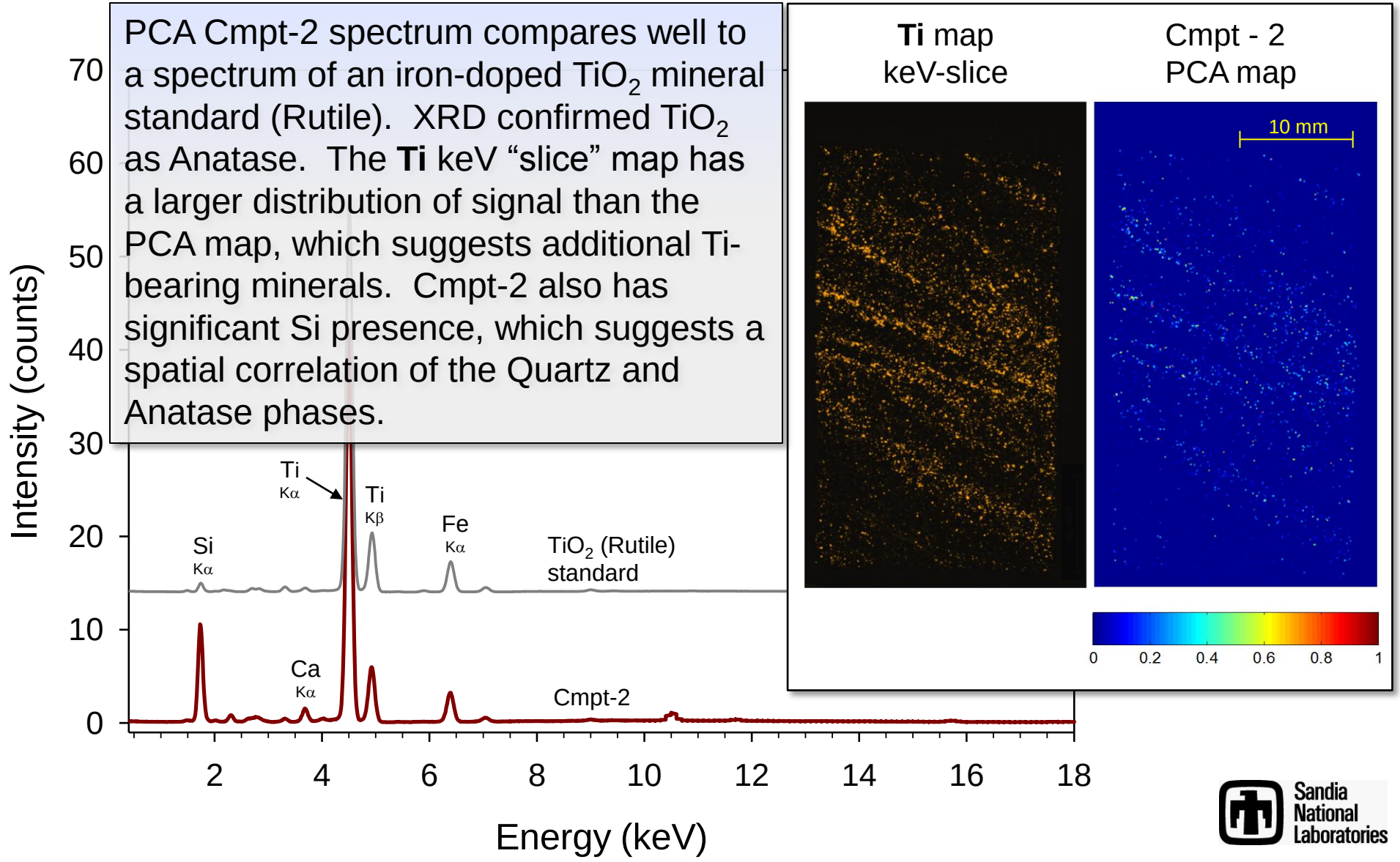
# Component 2
# Anatase

PCA Cmpt-2 spectrum compares well to a spectrum of an iron-doped $TiO_2$ mineral standard (Rutile). XRD confirmed $TiO_2$ as Anatase. The **Ti** keV "slice" map has a larger distribution of signal than the PCA map, which suggests additional Ti-bearing minerals. Cmpt-2 also has significant Si presence, which suggests a spatial correlation of the Quartz and Anatase phases.







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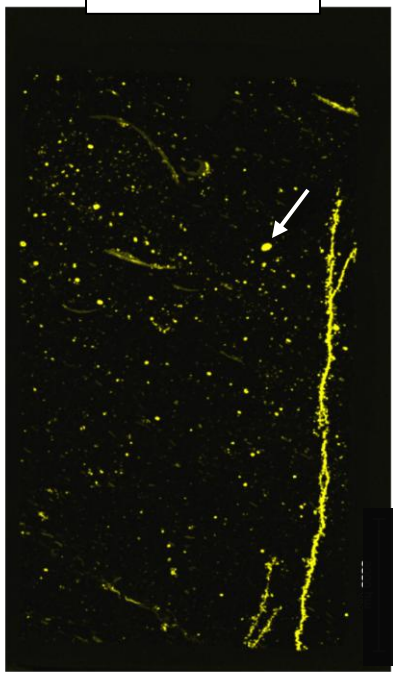
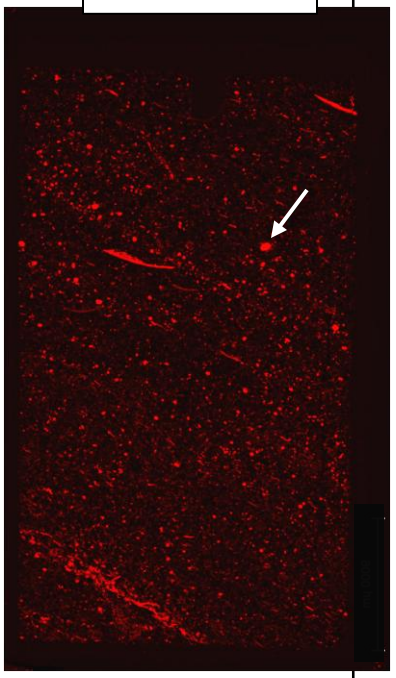
# Component 4 Pyrite

Cmpt-4 spectrum matches $FeS_2$ (Pyrite). XRD confirmed Pyrite as a trace phase. The PCA map shows Pyrite as isolated grains. The **Fe** and **S** keV "slice" maps can not distinguish Pyrite from other **Fe** or **S** bearing minerals.

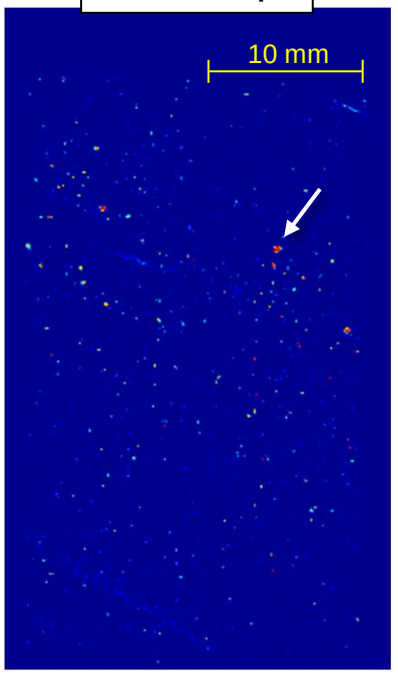
**S** map keV-slice

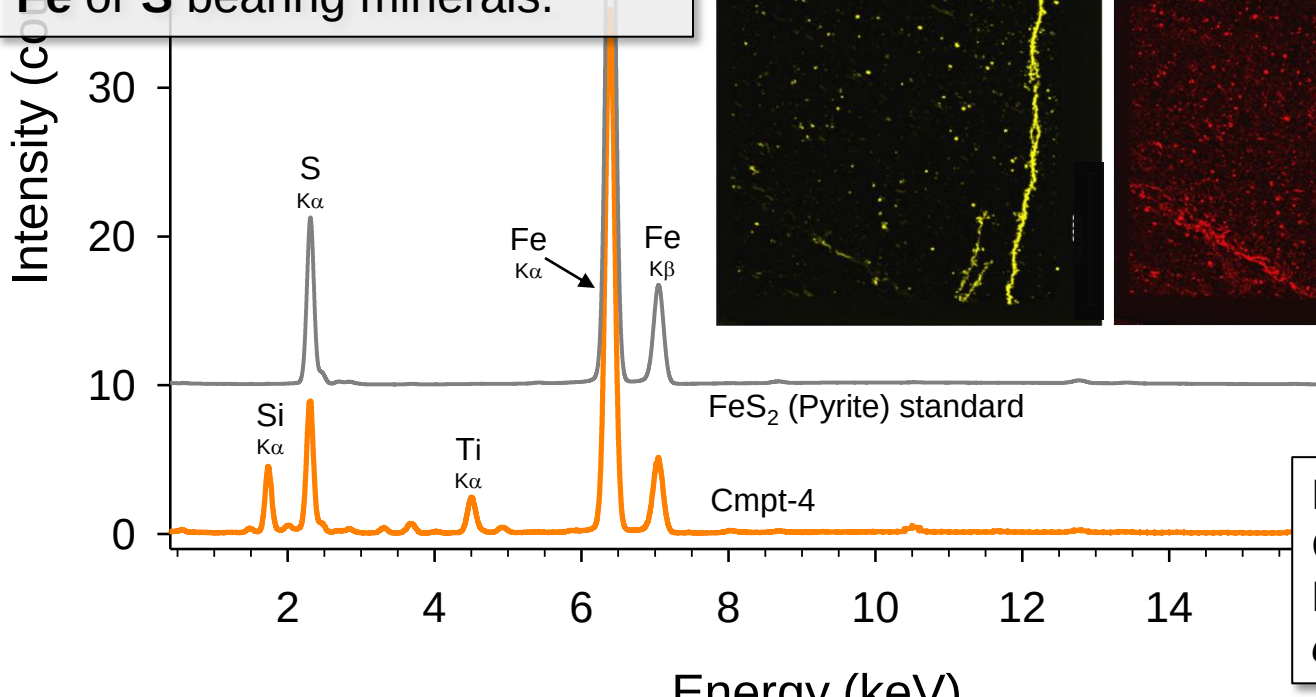


**Fe** map keV-slice



Cmpt - 4 PCA map




$FeS_2$ standard confirms Cmpt-4 as correct 1:2 Fe:S ratio. ***PCA-derived cmpts are quantitative.***

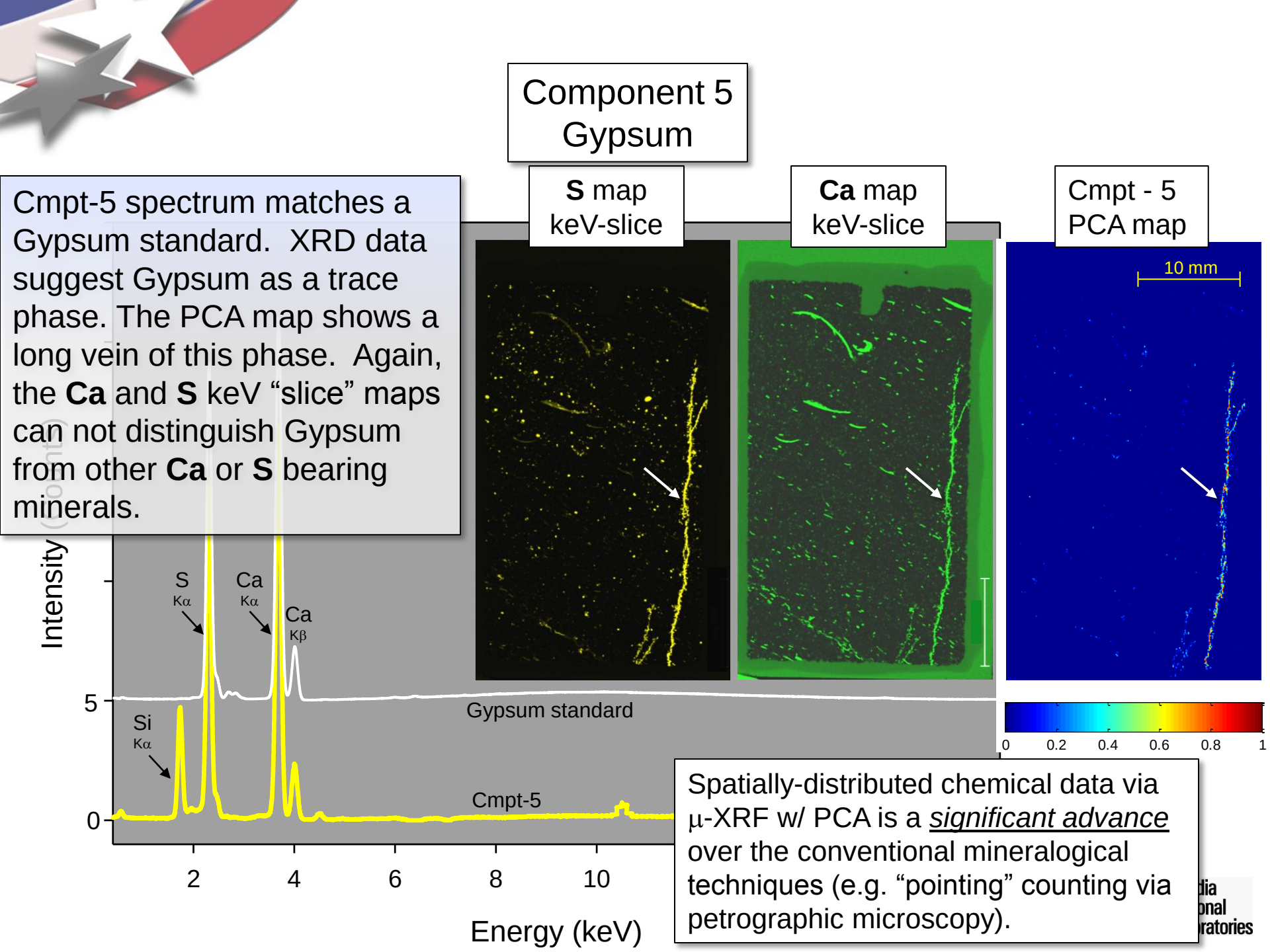
# Component 5 Gypsum

Cmpt-5 spectrum matches a Gypsum standard. XRD data suggest Gypsum as a trace phase. The PCA map shows a long vein of this phase. Again, the **Ca** and **S** keV "slice" maps can not distinguish Gypsum from other **Ca** or **S** bearing minerals.

**S** map keV-slice

**Ca** map keV-slice

Cmpt - 5 PCA map




Spatially-distributed chemical data via μ-XRF w/ PCA is a *significant advance* over the conventional mineralogical techniques (e.g. "pointing" counting via petrographic microscopy).

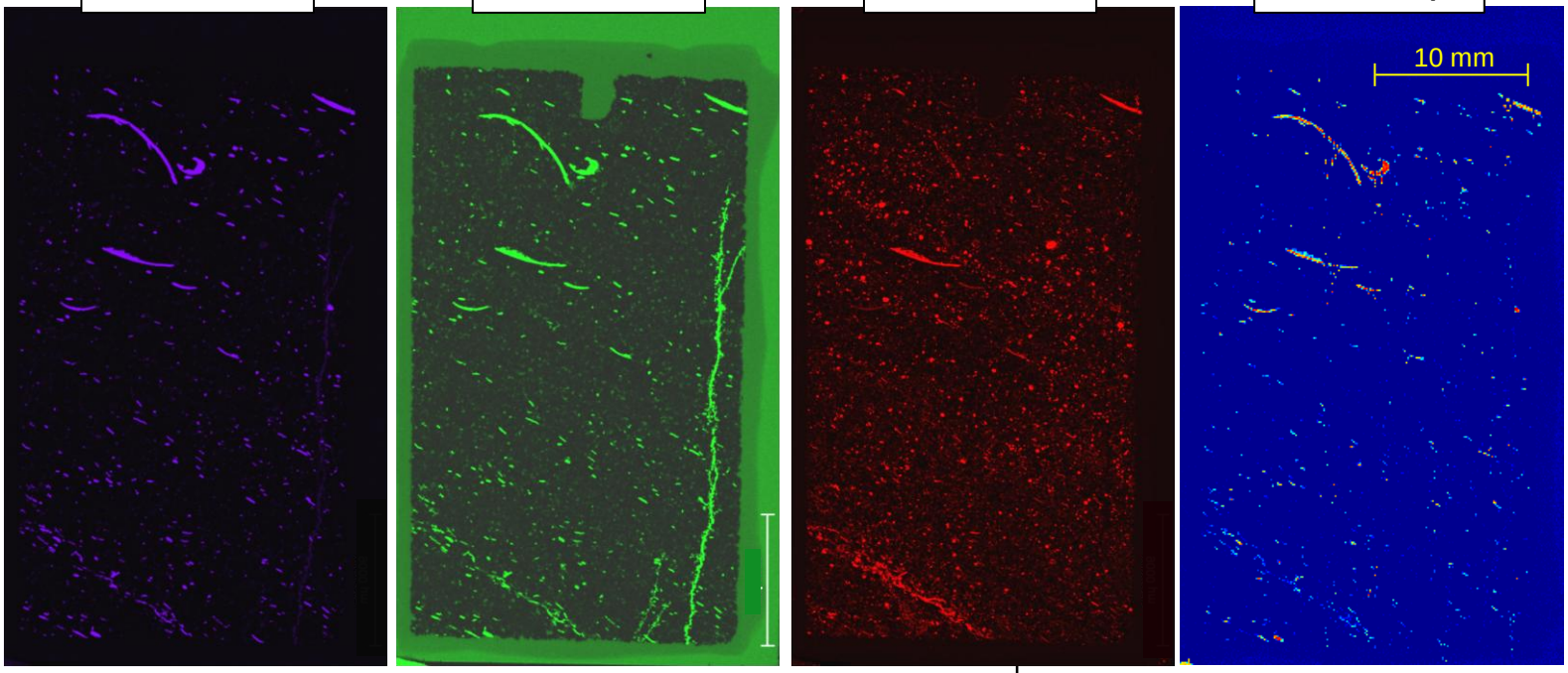
# Component 6
# Hydroxylapatite

**P** map
keV-slice

**Ca** map
keV-slice

**Fe** map
keV-slice

Cmpt - 6
PCA map







Cmpt-6 best matches Hydroxylapatite. Its presence was confirmed in the XRD pattern. Interestingly, the Fe map shows correlation to bone fragments as well.

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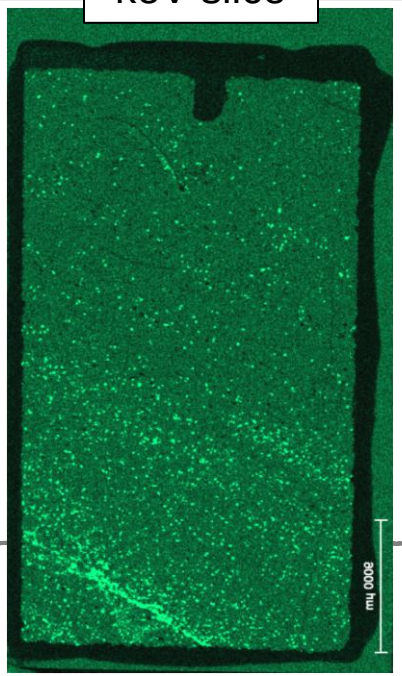
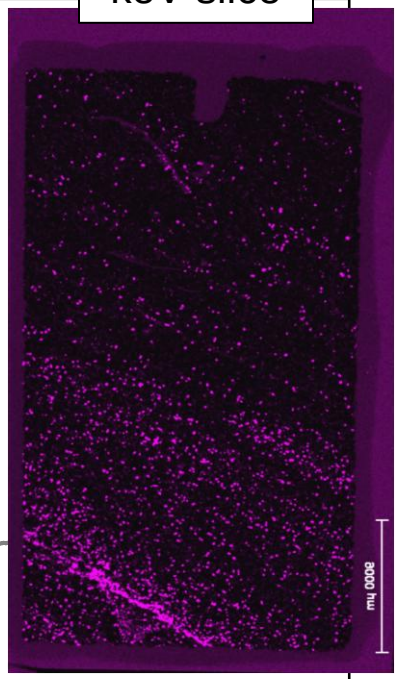
# Component 8
# Microcline / Orthoclase

Cmpt-8 spectrum matches a Microcline standard. XRD data confirm Microcline and Orthoclase phases. The PCA map easily isolates this phase while the Al and K maps are contaminated by the glass slide under the cross-section.

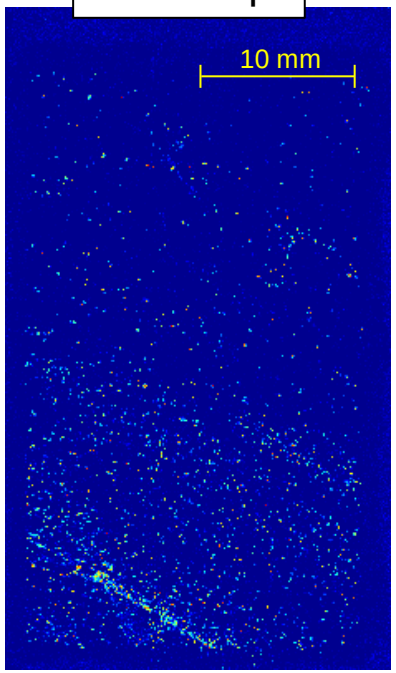
**Al** map keV-slice

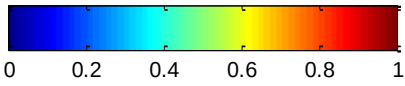


**K** map keV-slice



Cmpt - 8 PCA map







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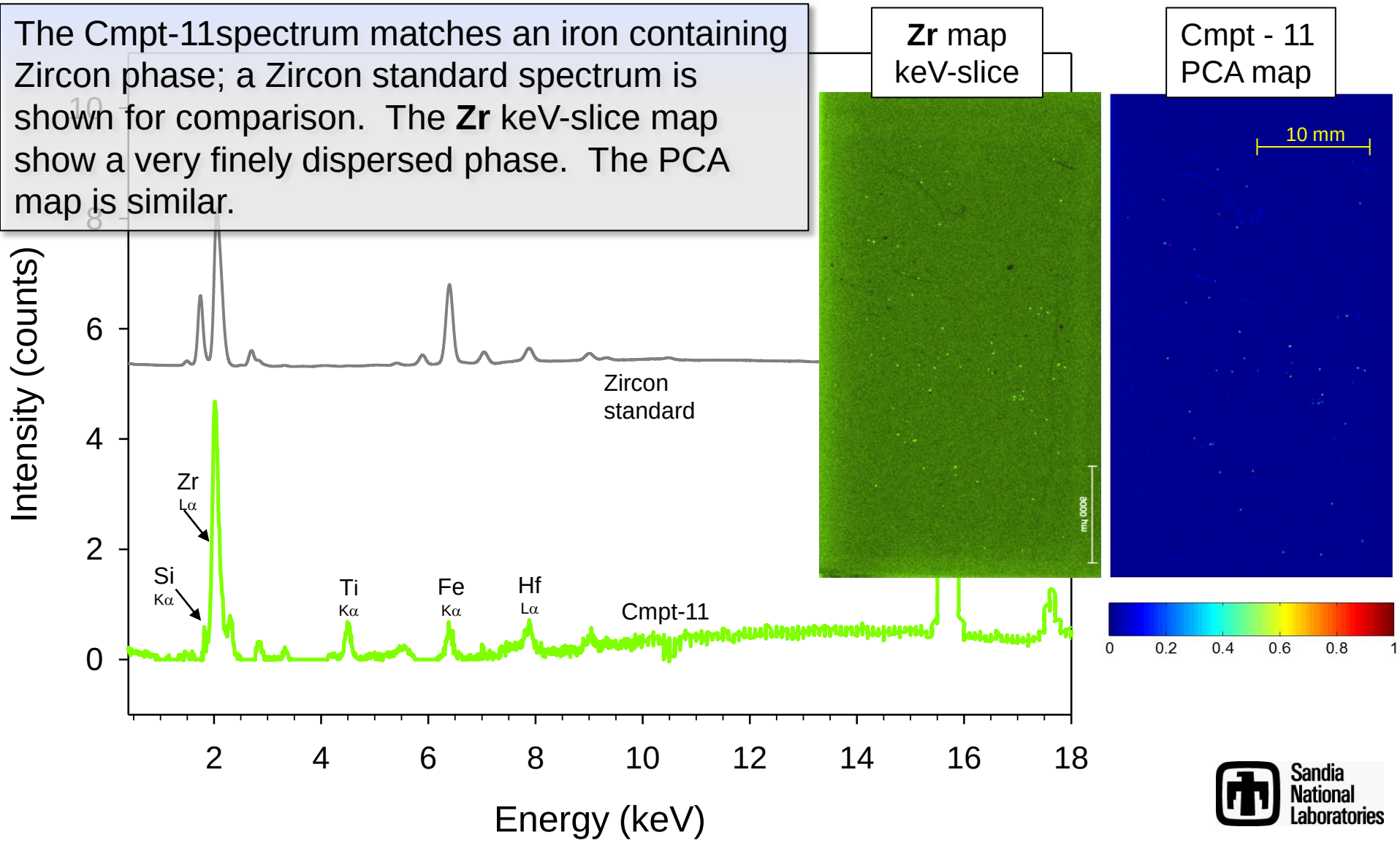
# Component 11
# Zircon

The Cmpt-11spectrum matches an iron containing Zircon phase; a Zircon standard spectrum is shown for comparison. The **Zr** keV-slice map show a very finely dispersed phase. The PCA map is similar.

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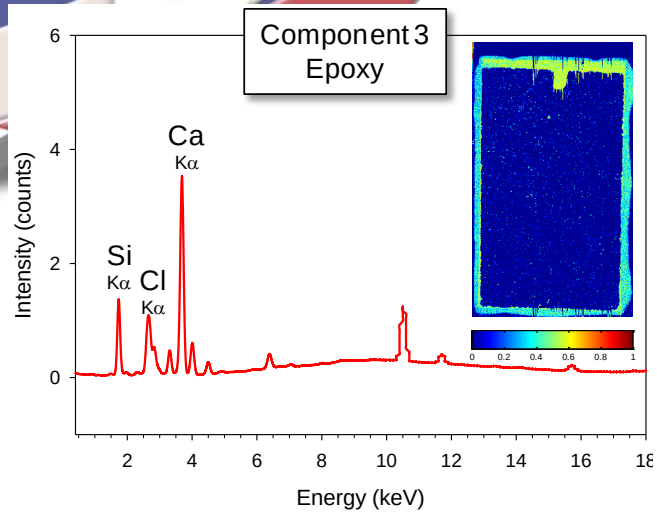
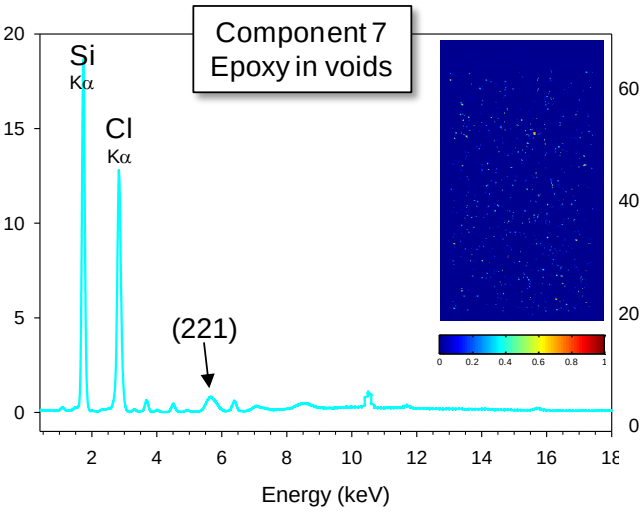
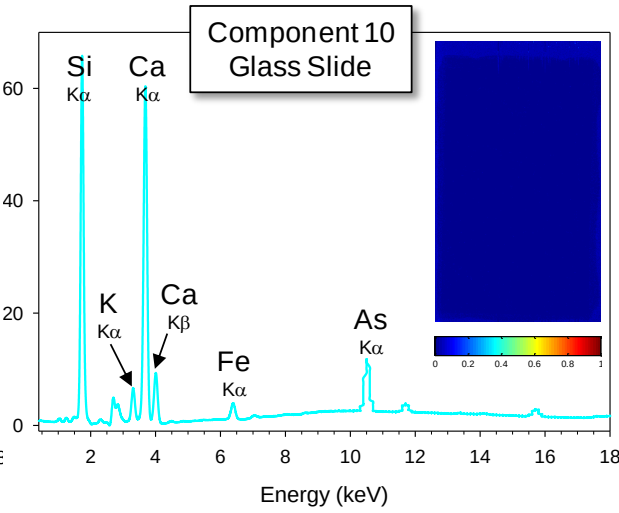
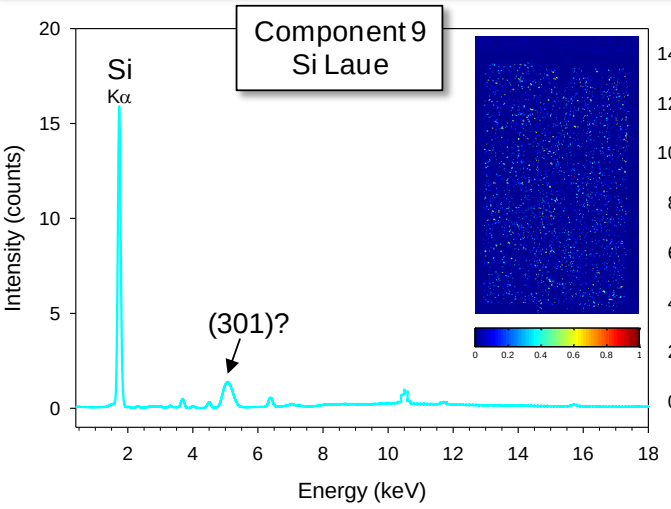
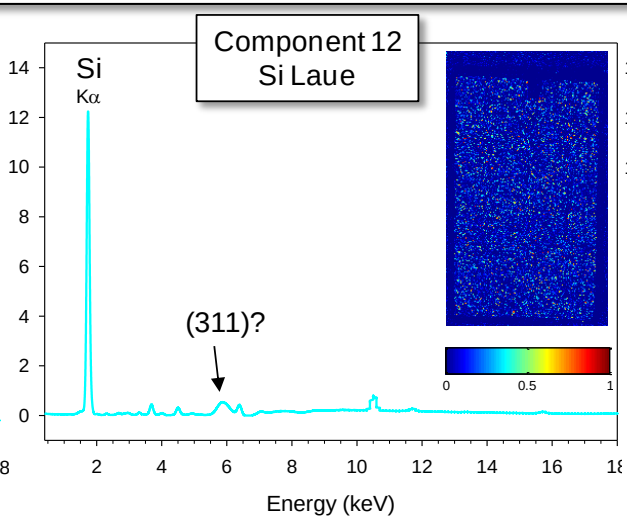


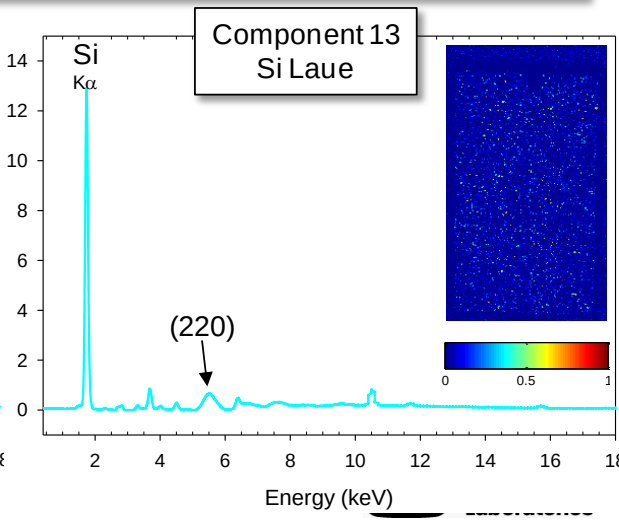



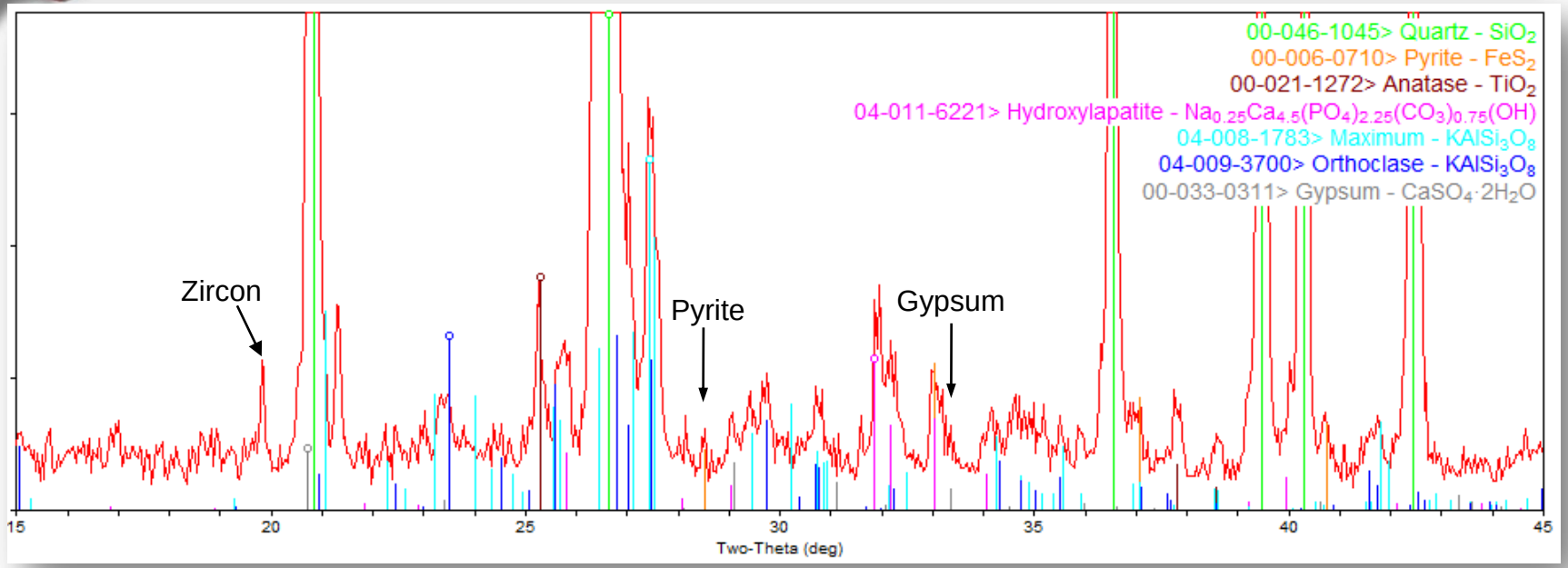

Additional PCA derived Components 3 and 7 relate to the Cl-containing epoxy-resin used to secure the cross-section to the underlying glass slide. Component 10 is from the glass slide itself. Components 9, 12, and 13 show strong **Si** signal along with Laue diffraction peaks. The PCA maps for these components indicate diffracting Quartz grains responsible for the observed energy-dispersive diffraction peak. It is possible to index the hk$\ell$ based on the diffracted energy value.



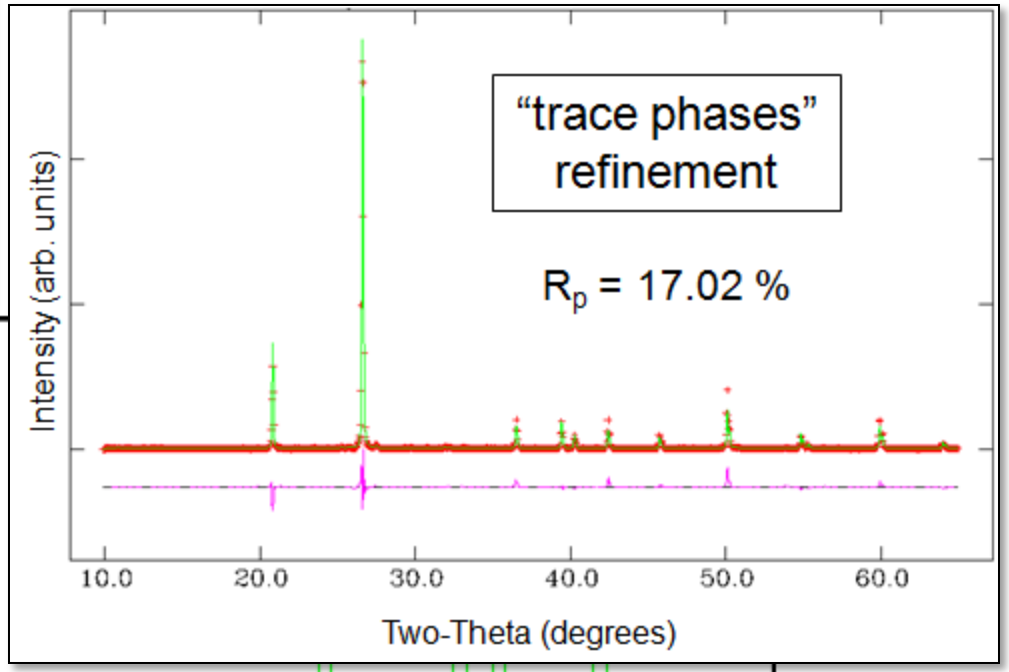



# PCA-aided identification of trace phases in XRD pattern.




Pyrite and Gypsum phases were ***very hard to detect*** by XRD alone, due to significant peak overlap and low intensity of the trace phases. PCA was vital for the confirmation of these important geological phases. The low quantity and isolation of Pyrite allayed concerns of $FeS_2$ oxidation that could lead to production of acid or lower pH during CAES.

New XRD Rietveld refinement including trace phases shows improved fitting of small peaks near background. The $R_p$ for the refinement reduced 1.5%.







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# Summary

- PCA analysis of μ-XRF datasets revealed a **highly-detailed**, spatially-constrained, set of components.
- Detection of **trace** phases in the core-drilled cross-section was greatly enhanced by PCA analysis.
- Derived PCA components are **quantitative** for the purpose of chemical composition determination.
- PCA augmented μ-XRF analysis generates within **seconds**, the same spatially-distributed chemical information as obtained through hours of labor-intensive petrographic microscopy.
- Results support geological characterization of the **renewable energy** site for CAES.
- Due to the low quantity measured, Pyrite oxidation is **not** a major concern during CAES operation.

## Acknowledgments


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