ZIRCONIUM-RICH URANINITE FROM THE CENTRAL CITY DISTRICT, GILPIN COUNTY, COLORADO

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Outline

- **Background**
- Objectives
- Sample locality and geology
- Analytical methods
- Sample petrography
- Chemical compositions
- Conclusions

Background

- Performance assessment (PA) of a spent nuclear fuel (SNF) repository in an oxidizing environment requires understanding of long-term behavior of the UO_2 in SNF

- Fate of fission products and radionuclides is critical to PA

- UO_2 in SNF is unstable: U(IV) -> U(VI) in uranyl oxide hydrates, uranyl silicates, uranyl phosphates.
- Fission products and radionuclides released from SNF UO_2 may be incorporated into of secondary uranium phases

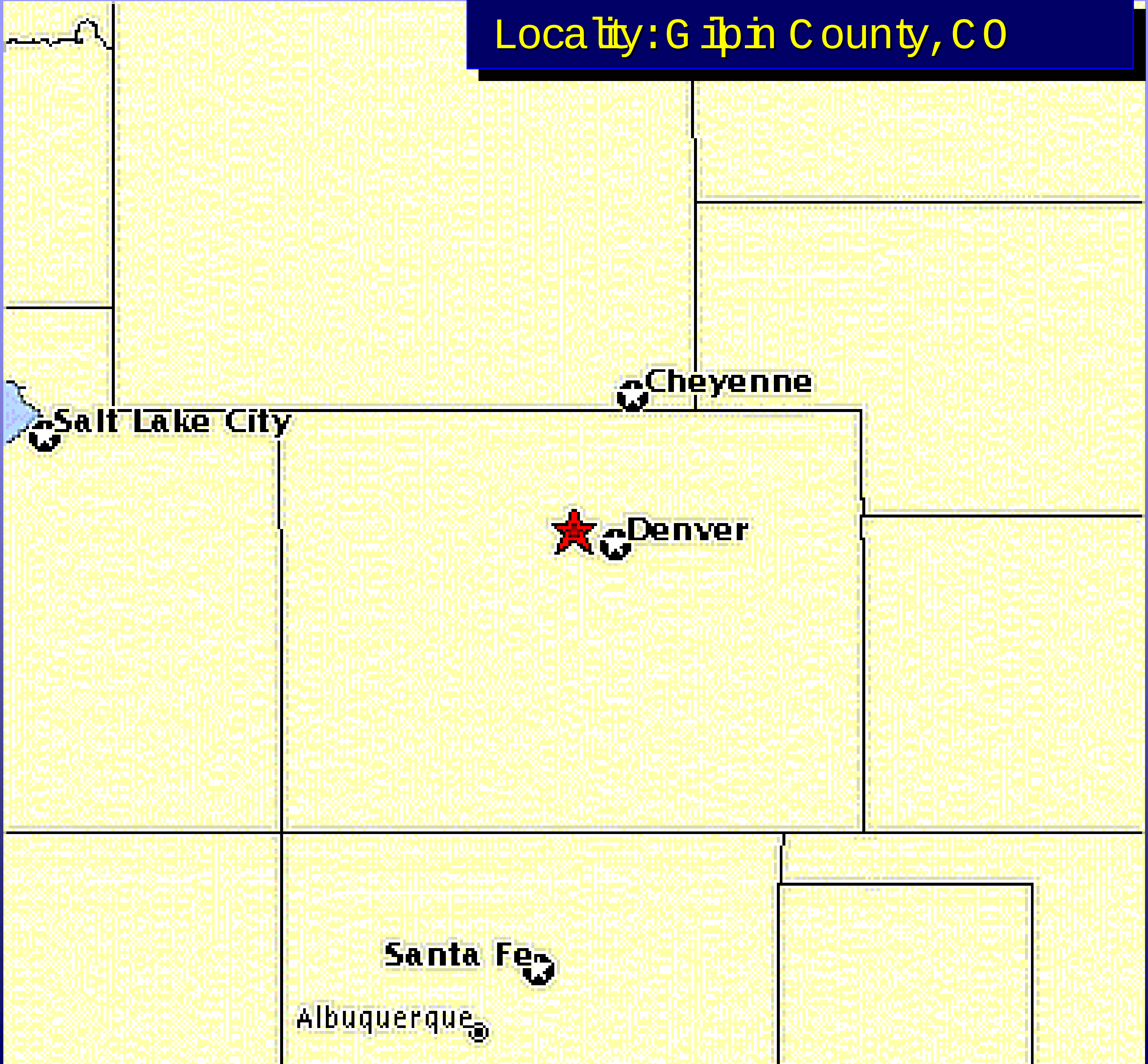
Natural Analogues

- Extrapolation of lab data to the long time period (10^3-10^5 years)
- Natural uraninite UO_{2+x} with its impurities is a good structural and chemical analogue for the long-term behavior of the UO_2 in SNF

Samples

- From the Central City District, Gilpin County, Colorado
- In common with Yucca Mountain, i.e., relatively arid environment
- Uranium mineralization is young: 40 to 2 Ma (Late Tertiary)
- High impurity content: Zr and Si

Locality: Gilpin County, CO



Geological Setting

- Uraninite occurs in arkosic rocks (alkali feldspar sandstone)
- Country rocks: Precambrian granite gneiss, schist and calc-silicate rocks cut by Tertiary granite, quartz monzonite, granodiorite and bostonite
- Bostonite dikes: rich in alkali feldspars, more radioactive, high uranium (up to 100 ppm)

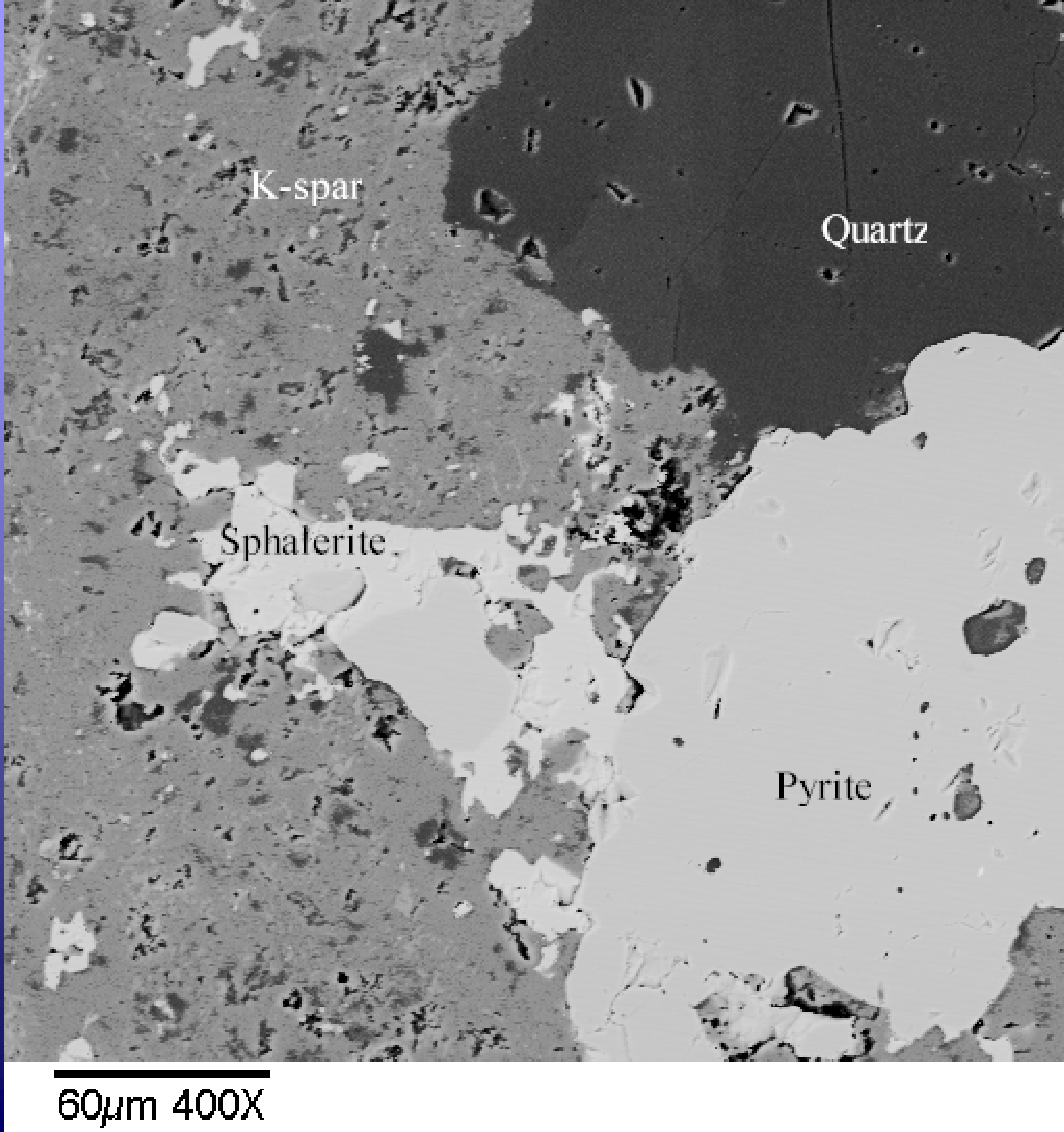
Analytical Methods

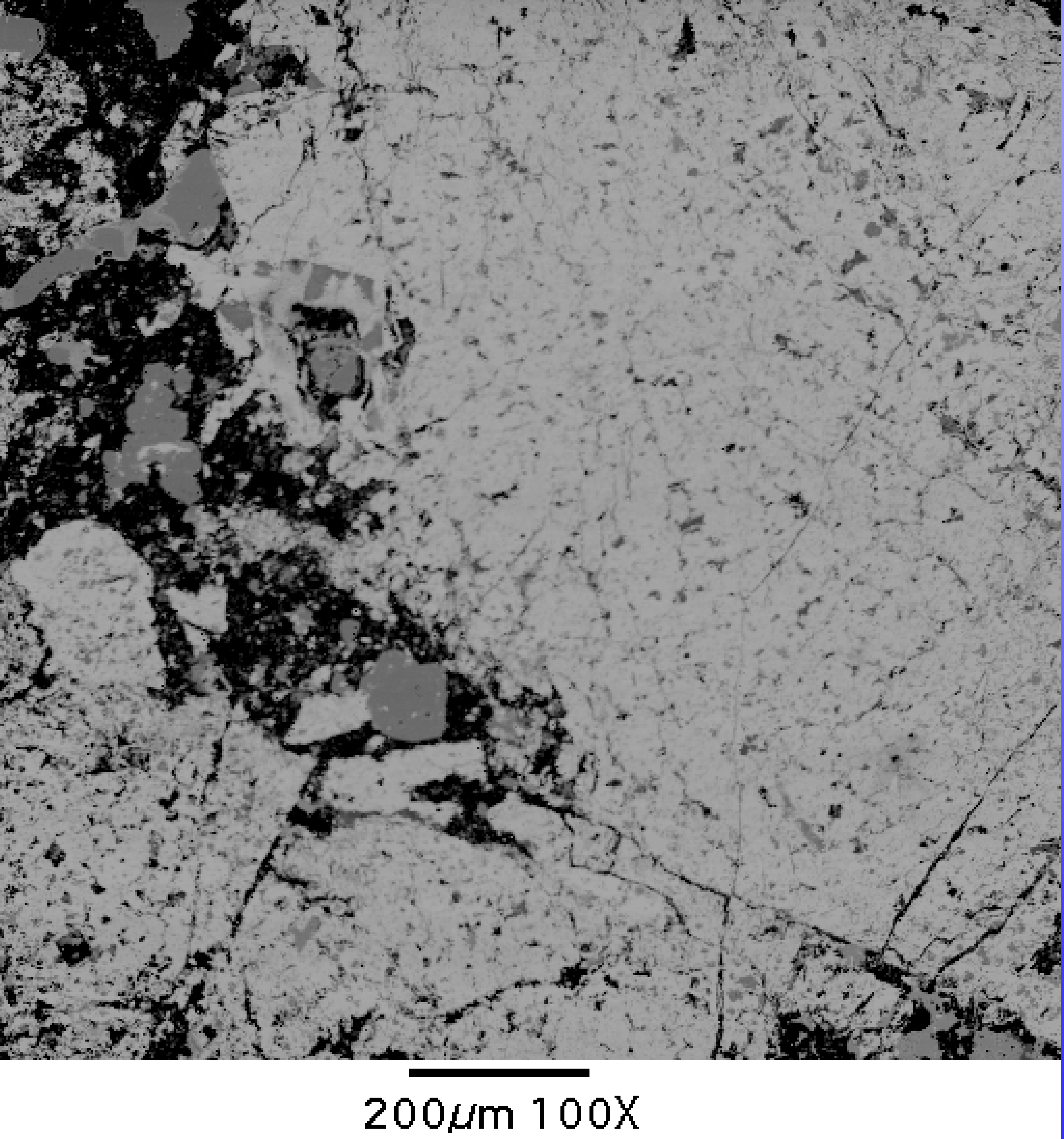
- Optical microscopy
- Scanning electron microscopy (SEM)
- Electron microprobe analysis (EMPA)
- Back scattered electron (BSE)
- Energy dispersive spectrum (EDS)

Petrography

- Uraninite/pitchblende
- Zr- and Si-rich uranium phase
- K-feldspar and albite $(K,Na)AlSi_3O_8$
- Quartz SiO_2
- Sulfides, e.g., pyrite FeS_2 and sphalerite ZnS

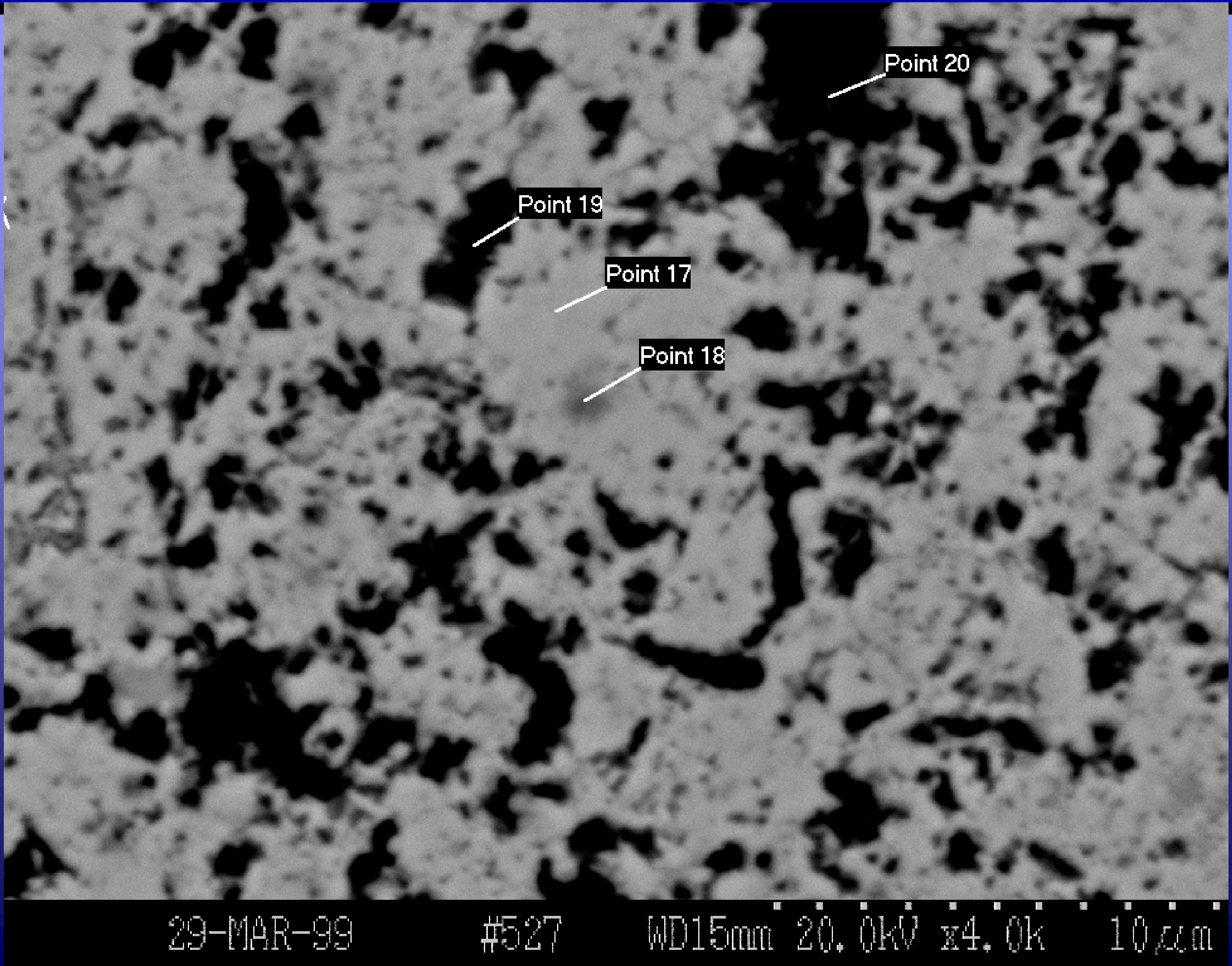
BSE image of host rock of the uraninite/pitchblende: K-feldspar $KAlSi_3O_8$, quartz SiO_2, and sulfides such as pyrite FeS_2 and sphalerite ZnS



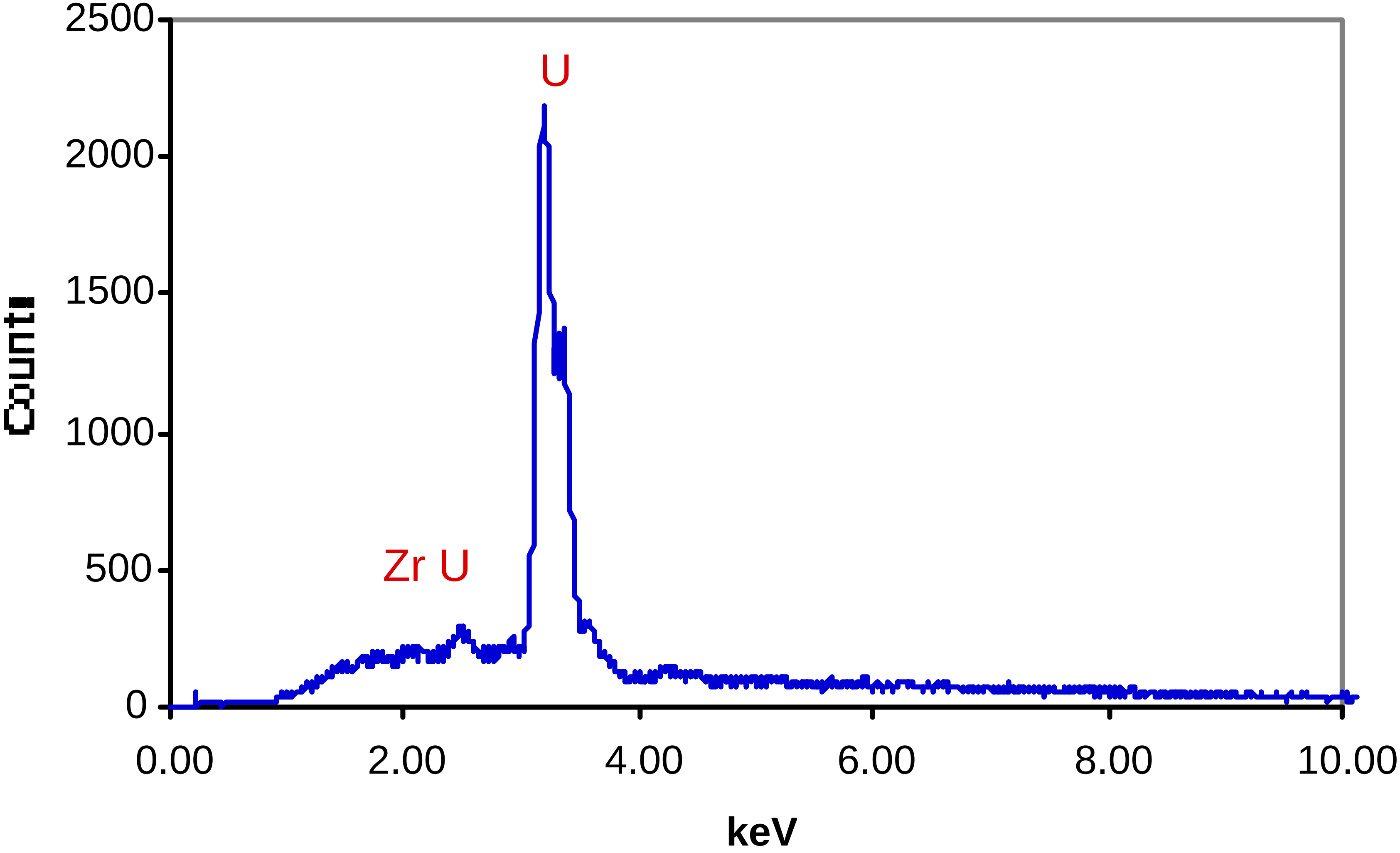


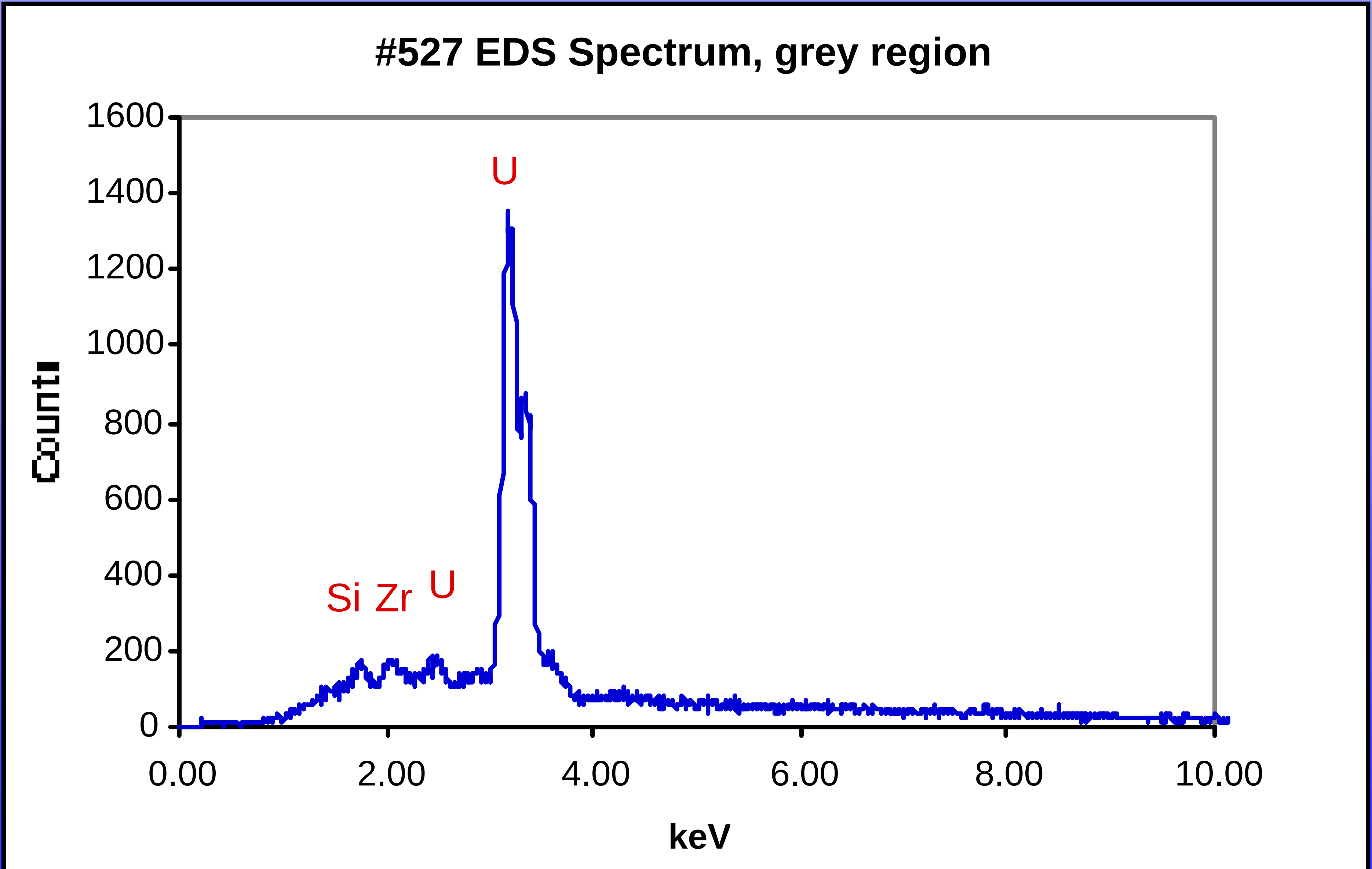
BSE image of Zr-rich uraninite with sulfides, K-feldspar, and quartz in microfractures

Point 17, bright, U; point 18, gray with U, Zr, Si and Fe; point 19, dark, more Zr and Si

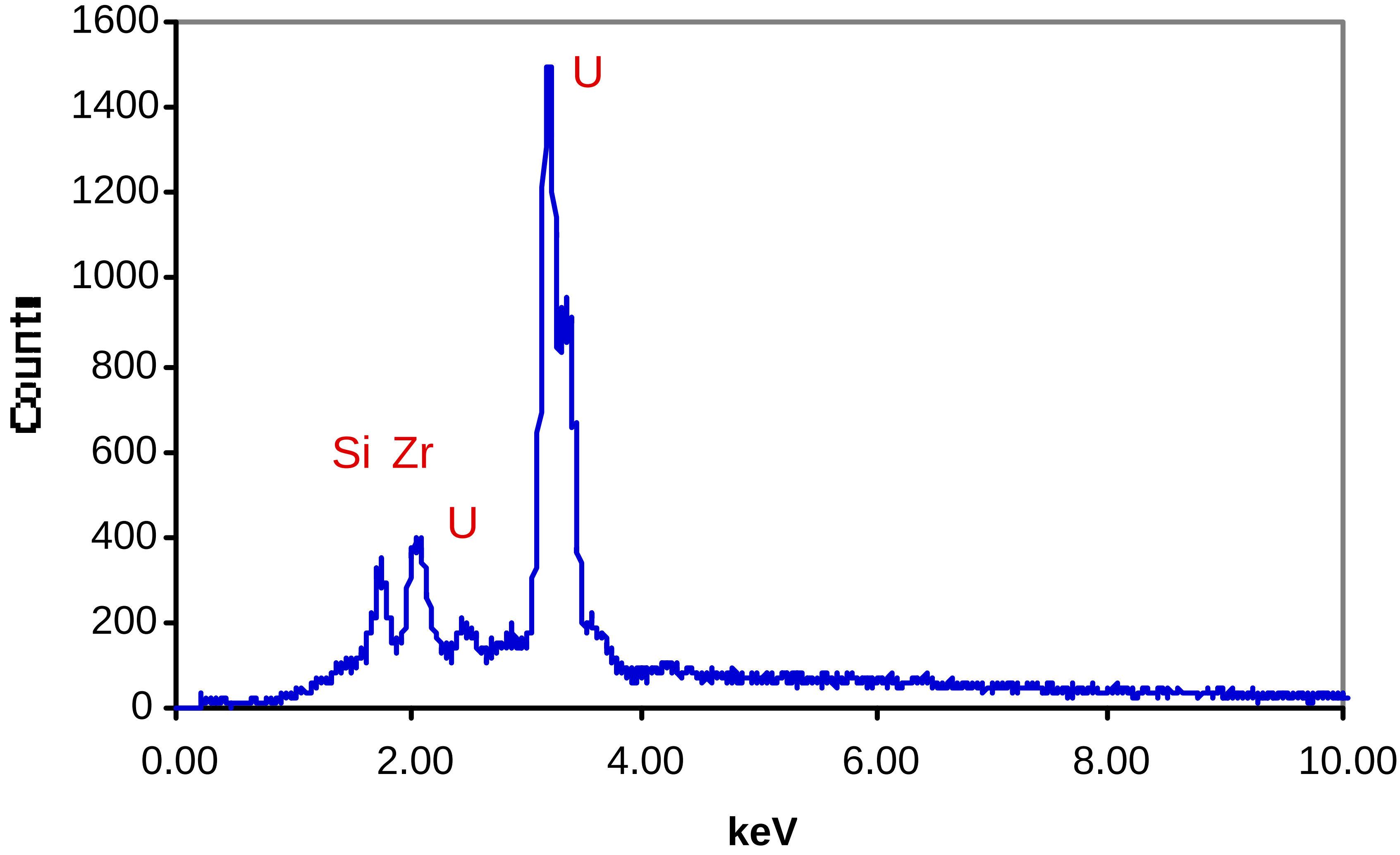


#527 EDS Spectrum, bright region




#527 EDS Spectrum, grey region
Counts
1600
1400
1200
1000
800
600
400
200
0
U
Si
Zr
U
0.00
2.00
4.00
6.00
8.00
10.00
keV

#527 EDS Spectrum, dark region



- Textural relationship suggests that the uraninite has altered partly and that Zr and Si were incorporated into the resultant uranium phases
- Si-enrichment indicates coffinitization
- Other alterations: silicification, sericitization and pyritization

EMPA conditions

- Cameca CAMEBAX EMP (WDS)
- Voltage: 20 kV
- Beam: 80 nA for Pb, U, Th; 20 nA for other elements
- Beam: spot mode or 3x3 μm^2 (for profile)
- Peak count time: 30 seconds
- Cameca PAP (modified ZAF)

Structural Formula

- $[U^{4+}_{1-x-y-z-u} U^{6+}_{x}(Th^{4+})_{u}REE^{3+}_{y}M^{2+}_{z}]O_{2+x-(0.5)y-z}$
- PbO to UO_2
- U^{4+} to U^{6+}, adding oxygen
- All U^{4+} converted to U^{6+}:
  - total > 100 wt %, both U^{4+} and U^{6+} exist
  - total < 100, H_2O and/or CO_2 may exist

Chemical Composition

- Heterogeneous
- UO_2 78.26 to 96.47 wt %
- PbO 0.52 to 5.27 wt %
- ZrO_2 1.09 to 8.28 wt %
- SiO_2 0.24 to 4.92 wt %

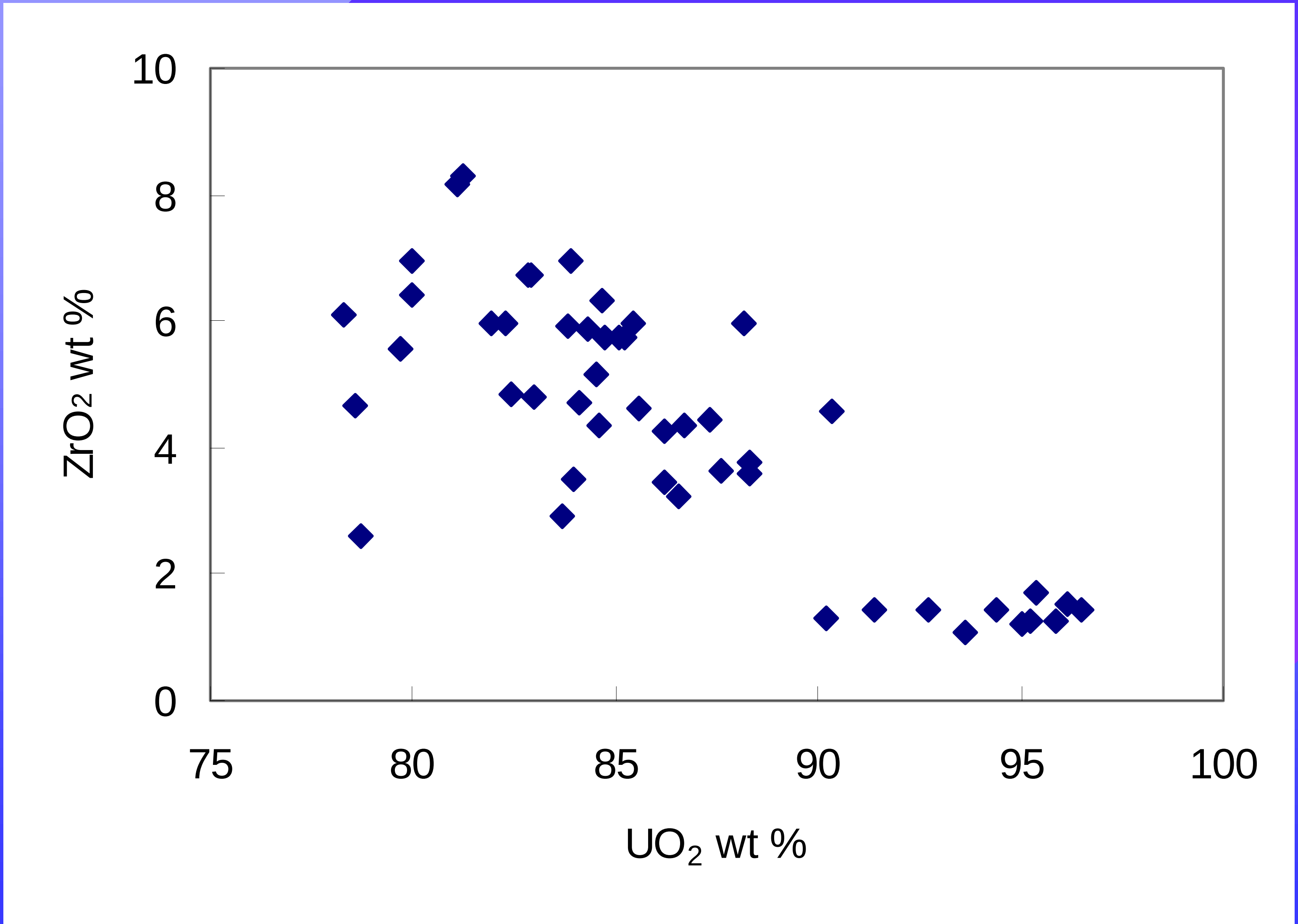
Trace Elements

- Low or below detection limits (b.d.l.)

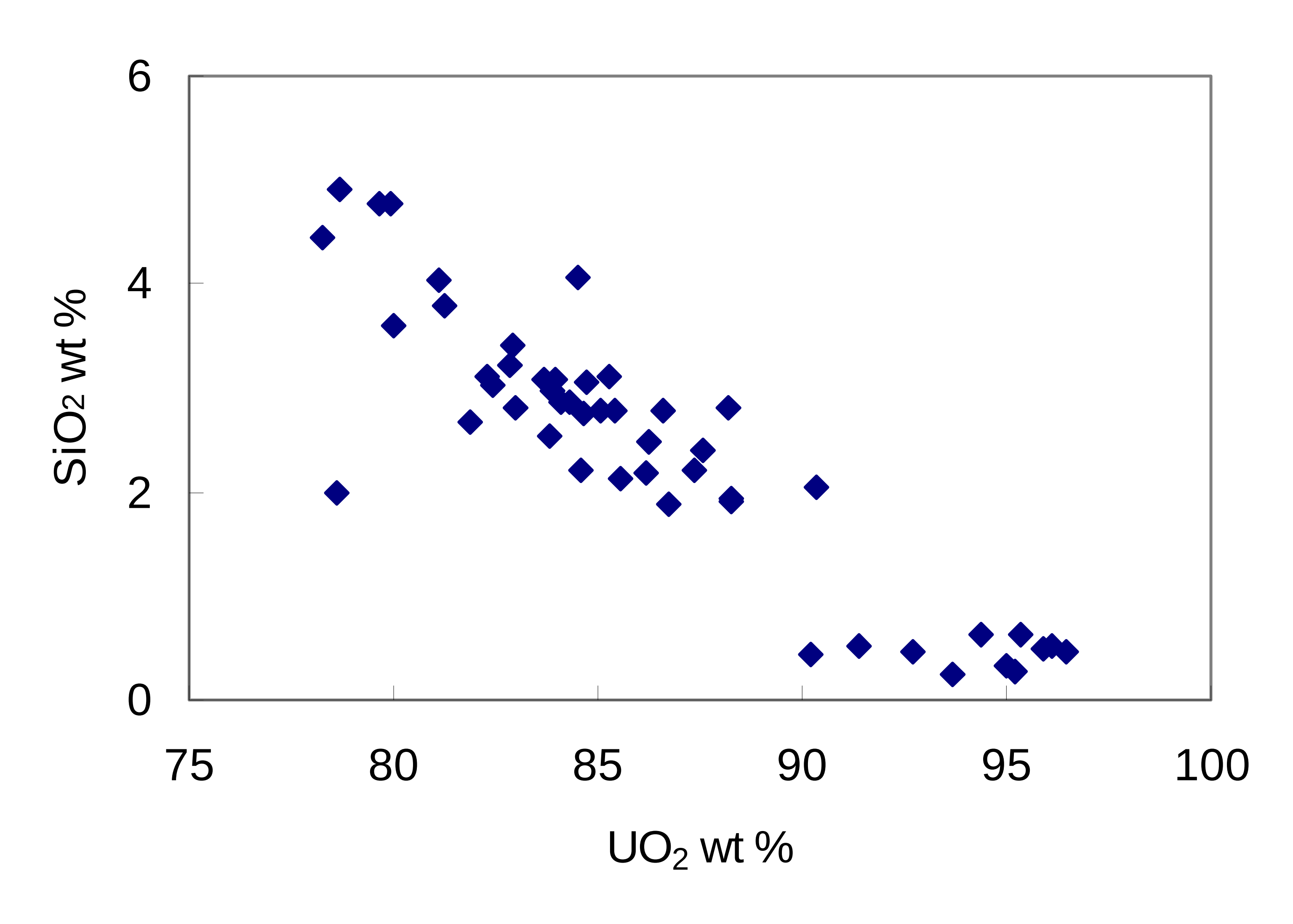
Oxide	*Average (wt %)*
Na_2O	b.d.l.
K_2O	0.29
MgO	0.02
MnO	0.09
TiO_2	0.14
SrO	b.d.l
SO_3	0.58
Y_2O_3	0.08

Oxide	*Average (wt %)*
La_2O_3	0.03
Ce_2O_3	0.08
Pr_2O_3	0.01
Nd_2O_3	0.02
Sm_2O_3	0.02
Eu_2O_3	0.01
Gd_2O_3	0.02
ThO_2	0.04

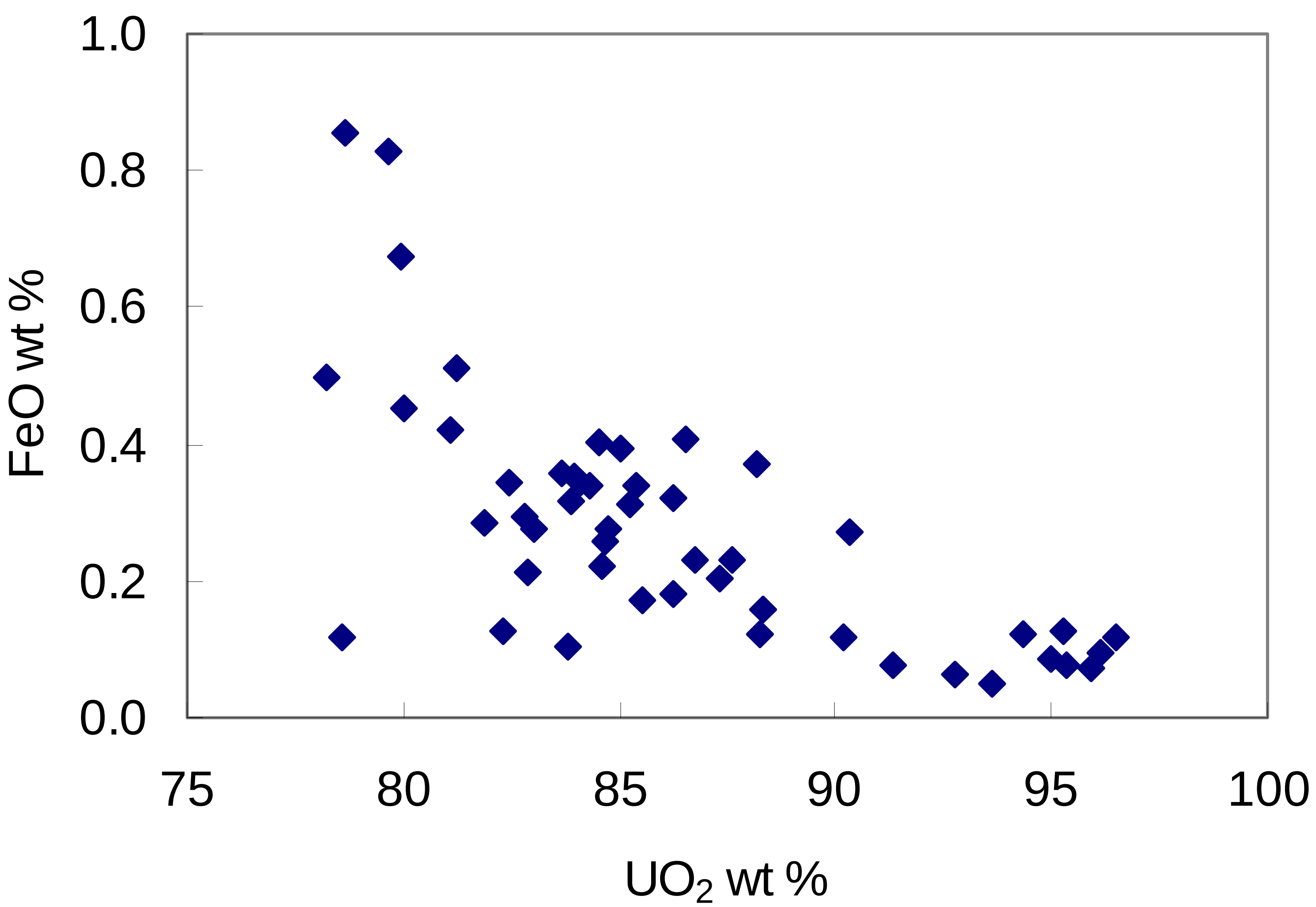
ZrO_2 in two areas; negative correlation between ZrO_2 and UO_2; pristine uraninite has higher UO_2 and lower ZrO_2; secondary uranium minerals contain lower UO_2 and higher ZrO_2



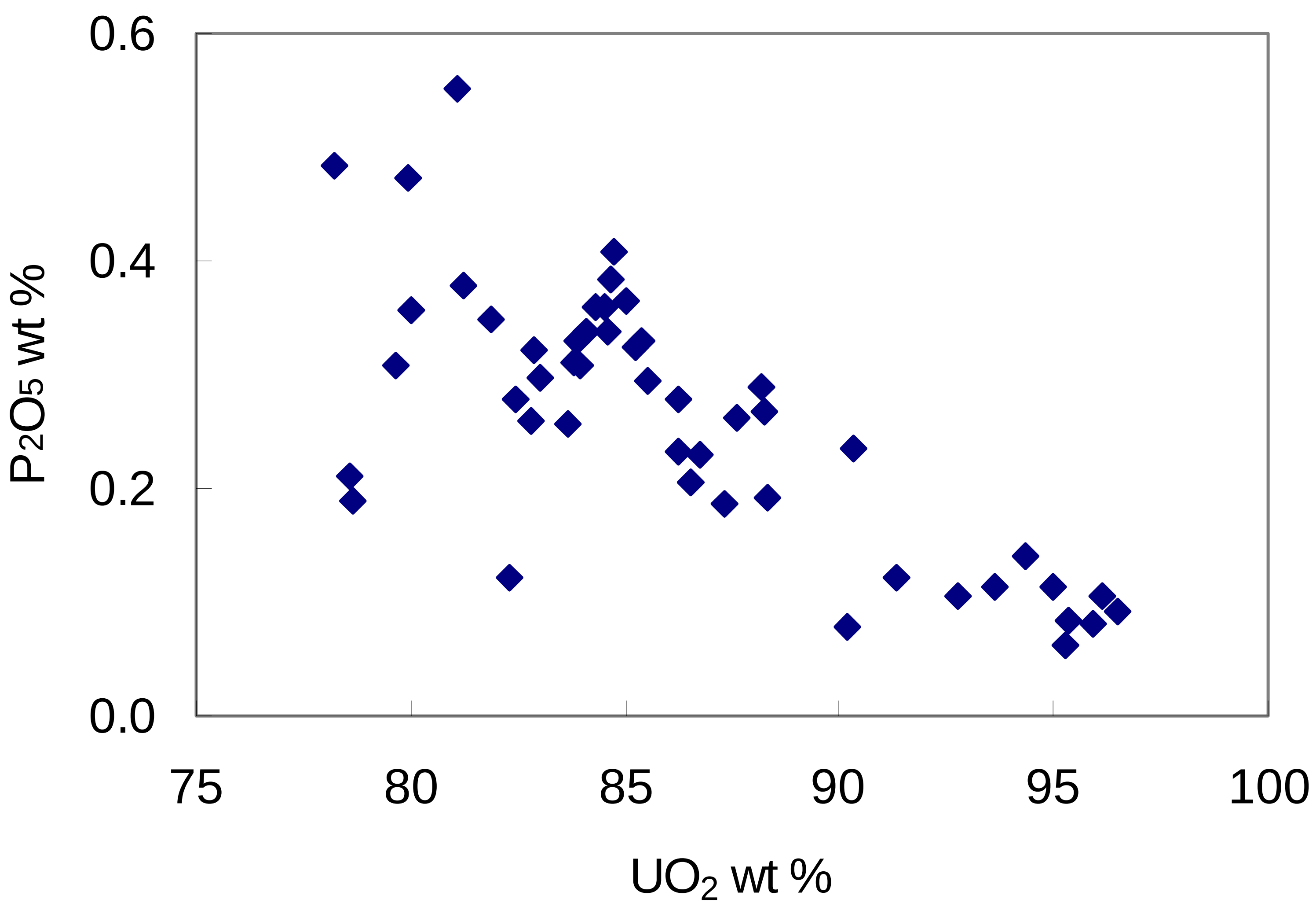
SiO_2 in two areas; negative correlation between SiO_2 and UO_2; pristine uraninite has higher UO_2 and lower SiO_2; secondary uranium minerals contain lower UO_2 and higher SiO_2



FeO contents increase with the decrease of UO_2



P2O5 contents increase with the decrease of UO_2

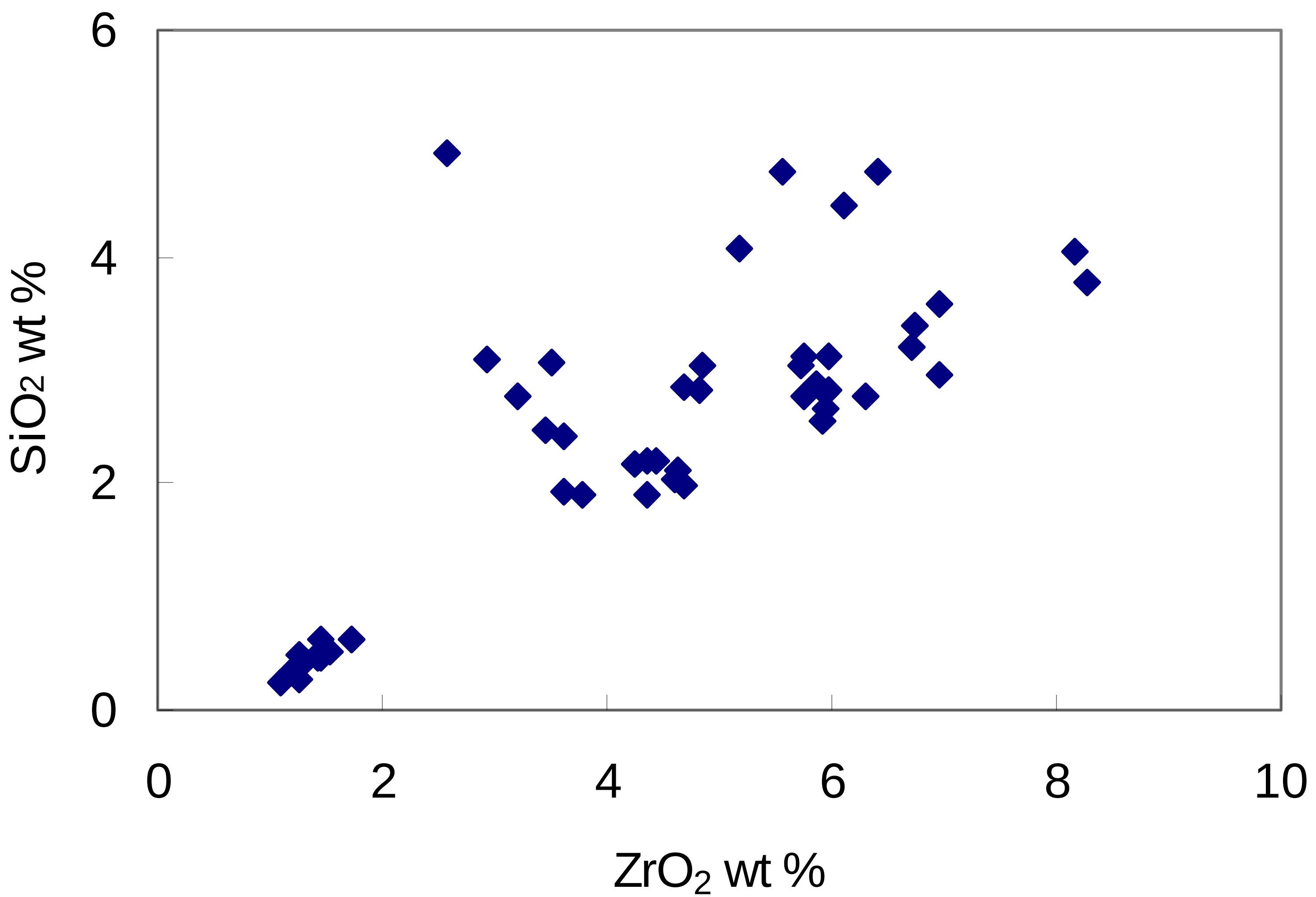


Compositional Differences

Oxide (wt %)	*Primary uraninite*	*Secondary Zr- and Si-rich region*
UO_2	90.2 to 96.5	78.3 to 90.4
ZrO_2	1.1 to 1.7	2.6 to 8.3
SiO_2	0.3 to 0.6	1.9 to 4.9

- **ZrO_2, SiO_2, FeO and P_2O_5 increase with decreasing UO_2 contents**
- **UO_2 indicate the oxidizing conditions of alteration**
- **Oxidization -> Zr, Si, Fe and P incorporation -> formation of uranium silicates or phosphates**
- **Uranium silicates or phosphates have high capability to incorporate trace elements, including fission products and radionuclides**

Positive correlation between ZrO_2 and SiO_2 seemly indicates that Zr and Si are from zircon $ZrSiO_4$, a common component in host or country rocks



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Conclusions

- BSE images and EDS show that the Zr- and Si-rich phase is adjacent to the primary uraninite
- Primary uraninite contains higher UO_2 and lower ZrO_2 and SiO_2
- Secondary Zr- and Si-rich region has lower UO_2 and higher ZrO_2 and SiO_2

Conclusions

- Alteration of the uraninite results in incorporation of Zr, Si, Fe and P, thus formation of uranium silicates or phosphates,
- Uranium silicates or phosphates have higher capability to incorporate fission products and radionuclides, thus could serve as a barrier
- Other trace elements are low or below detection limit