



**Study of organic-rich limestones of the Epirus region
(Greece) using nuclear and synchrotron radiation
techniques.**

I. T. Tzifas, P. Misaelides

Dept. of Chemistry
ARISTOTLE UNIVERSITY
GR-54124 Thessaloniki

The objective of this work was the investigation of the organic-rich phosphatized limestones of the Epirus region.

According to previous geological surveys by GAEC and IGME, these limestones exhibit radiometric irregularities due to their U-content.

The identification of the U-bearing mineral phases of the limestones using microscopic-, spectroscopic-, atomic-, nuclear and synchrotron radiation techniques was one of the main tasks of this study.

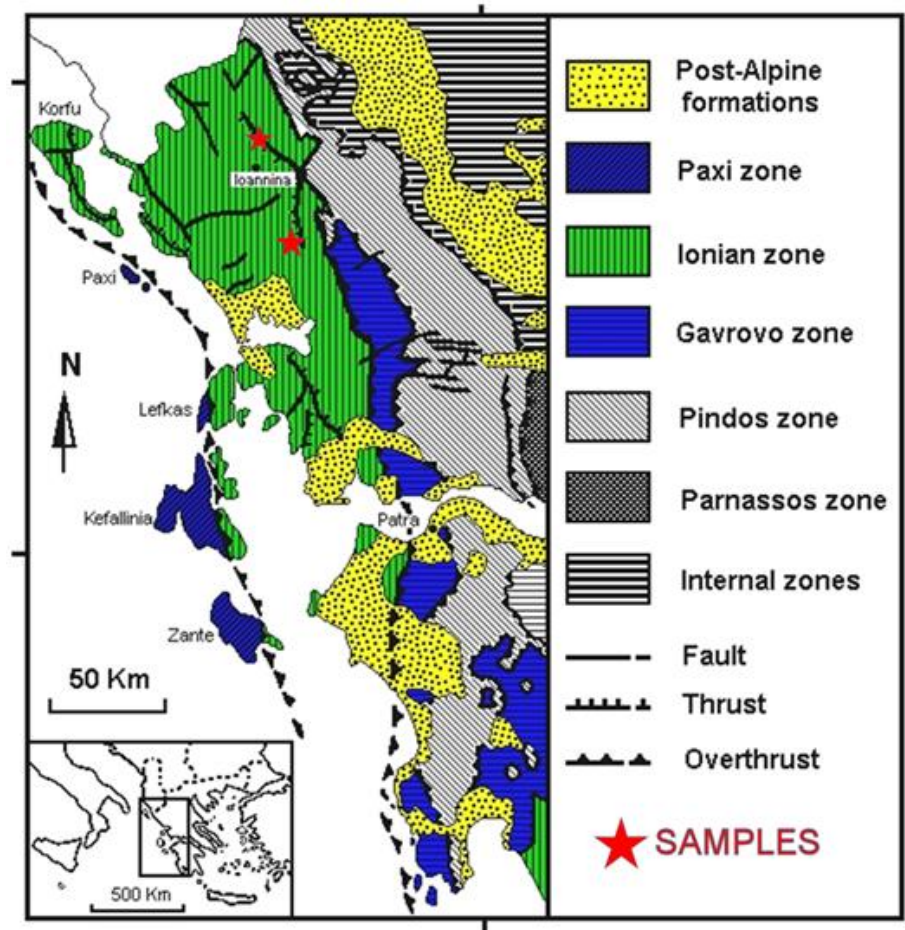
The data of this presentation were obtained within the frame of I.T. Tzifas' PhD Thesis, which is still in progress (Subject: **Distribution of natural actinides (Th, U) in greek rare-earth element bearing geologic materials**).

Sampling region:

The sampling locations were selected on the basis of surveys the suspected Mesozoic* sedimentary formations by means of a portable radiation counter with a NaI(Tl) detector.

The studied geological formations belong to Ionian geotectonic zone which is mainly characterized by the presence of carbonate rocks.

The specimens presenting enhanced radiation consisted of phosphatized limestones partially rich in organic matter.



* Mesozoic: 252-66 Million years old

Treatment and separation of the samples:

After crushing, pulverization by milling and washing of the samples, heavy mineral separation was carried out in four steps in order to obtain concentrates of apatite crystals, which are potential hosts of uranium:

- heavy liquid separation using 80 % sodium polytungstate (density: 2.8 kg/m³)
- magnetic separation of the >2.8 kg/m³ fraction using a Frantz magnetic separator
- treatment of the non-magnetic fraction by a methylene iodide and acetone mixture (density: 3.2 kg/m³) in order to separate the apatite crystals and finally
- processing by pure methylene iodide (density: 3.3 kg/m³) to obtain the zircon (ZrSiO₄) microcrystals.

The separated inorganic phases were mainly:

calcite (CaCO₃)
apatites (Ca₅(PO₄)₃(F,Cl,OH))
and francolites (Ca₅(PO₄,CO₃)₃(F,OH)).

Secondary minerals present:

Zircons (ZrSiO₄)
Pyrite (FeS₂)
Hematite (Fe₂O₃)
Magnetite (Fe²⁺Fe³⁺₂O₄)

The matrix of the breccia consisted of cementing material (black organophosphate matter and calcite), but also of sand and/or silt sized clasts cemented together among the coarser clasts.

The Sample Characterization

```
graph TD; A[The Sample Characterization] --> B[Structural characterization]; A --> C[Chemical Analysis]; A --> D[Microscopy]; A --> E[Synchrotron radiation techniques]; A --> F[Fission tracks];
```

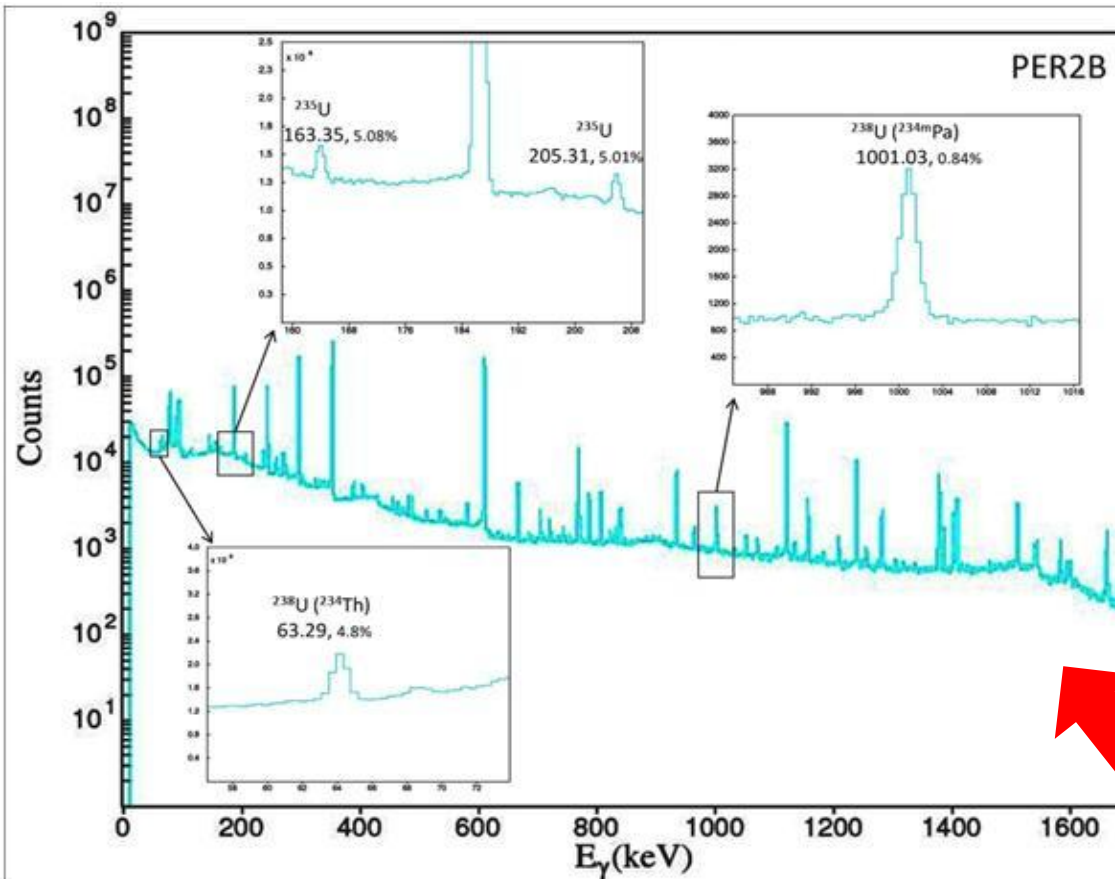
**Structural
characterization**

Chemical Analysis

Microscopy

**Synchrotron radiation
techniques**

Fission tracks



Representative γ -spectrum of the most active sample (activity: 7700 ± 425 Bq/kg).

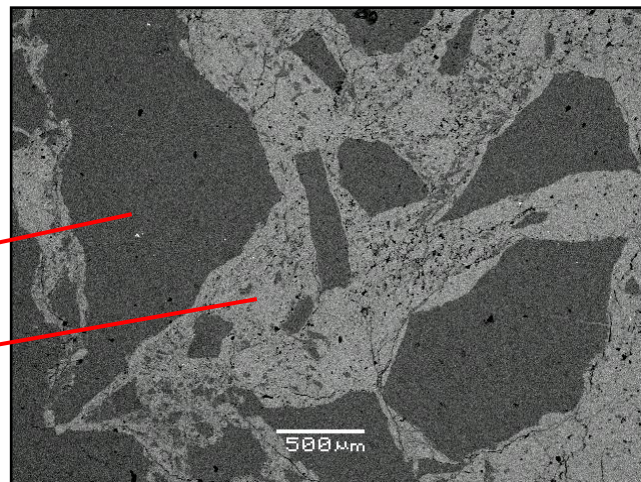
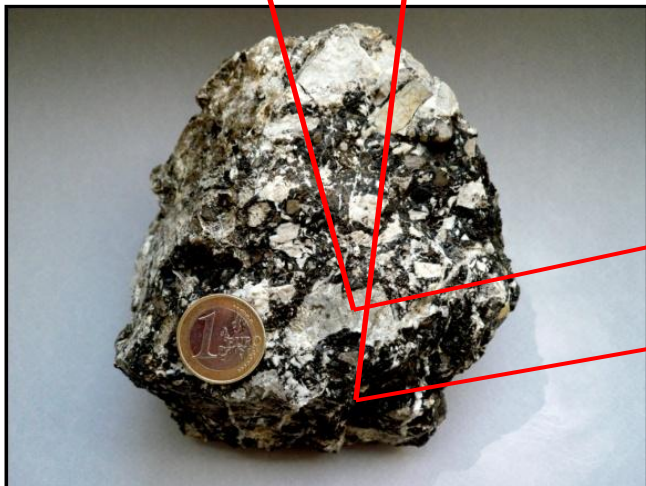
The high-resolution gamma-spectroscopy indicated the presence of uranium (s. photopeaks at 1001 (^{234m}Pa), and 609.3 keV (^{214}Bi) belonging to ^{238}U natural radioactive series).

Bulk chemical analyses using ICP-OES/MS showed variable U-concentration in the samples with a notable peak value of 648 ppm in the case of dark organic-rich material hosted into the phosphatized limestones of a sample collected in area of Perivleptos.

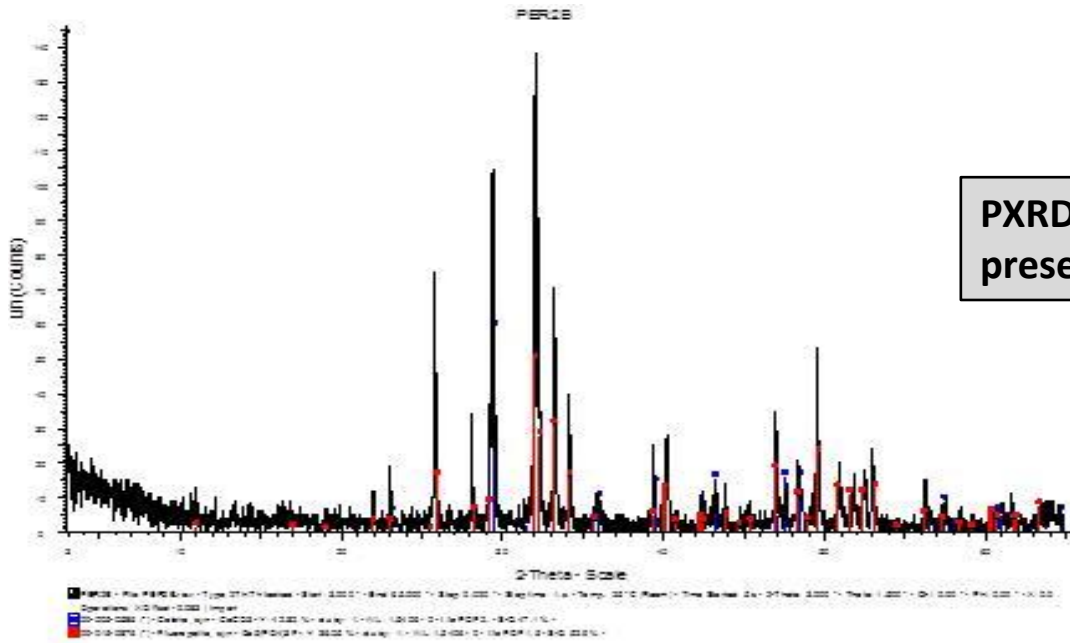
The U-content of the other collected samples was considerably lower.

	U(ppm)	K(ppm)	Th(ppm)
DRYM1	21,8697	125,97	0,2
PER1	3,5772	742,9	0,2
PER2A	7,1544	48,45	0,01
PER2B	626,01	1550,4	0,7

Calculated on the basis that
1 Bq kg⁻¹ of ²²⁶Ra or ²¹⁴Bi = 81.3 ppb U



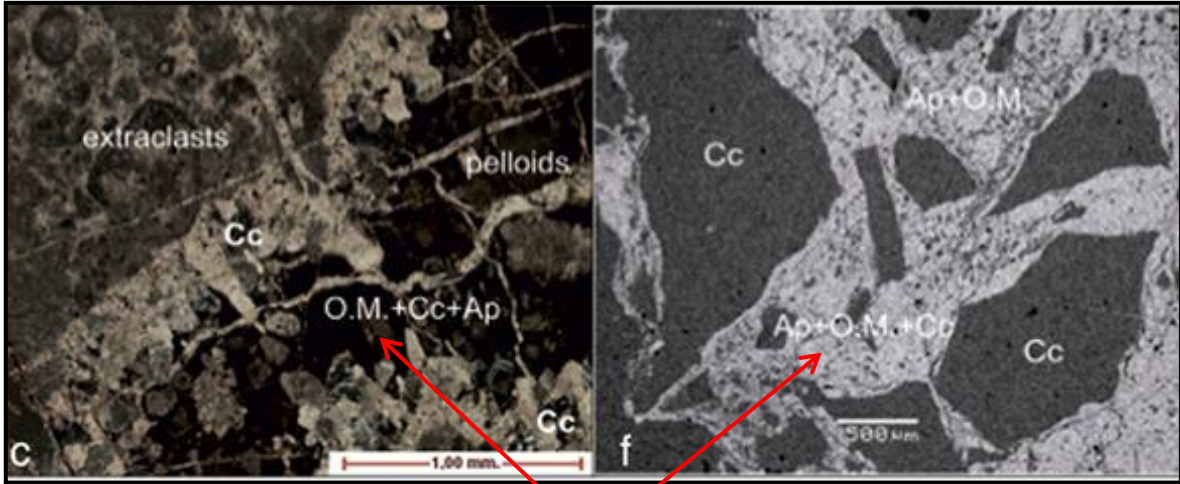
SEM-EDS examination of the samples combined with XRD showed that the main phases of the samples were apatite (fluoroapatite and carbonate apatite), calcite and organic matter.



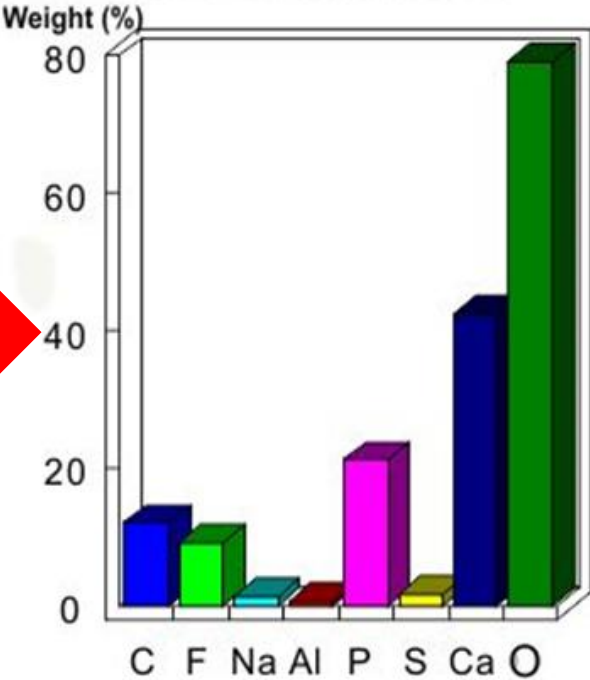
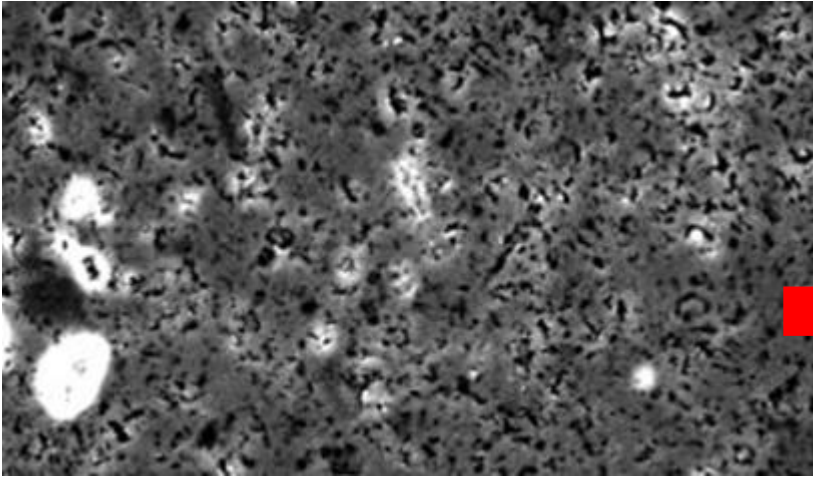
PXRD-pattern of PER2 Sample showing the presence of apatite and calcite.

**Optical and
Electron microscopy**

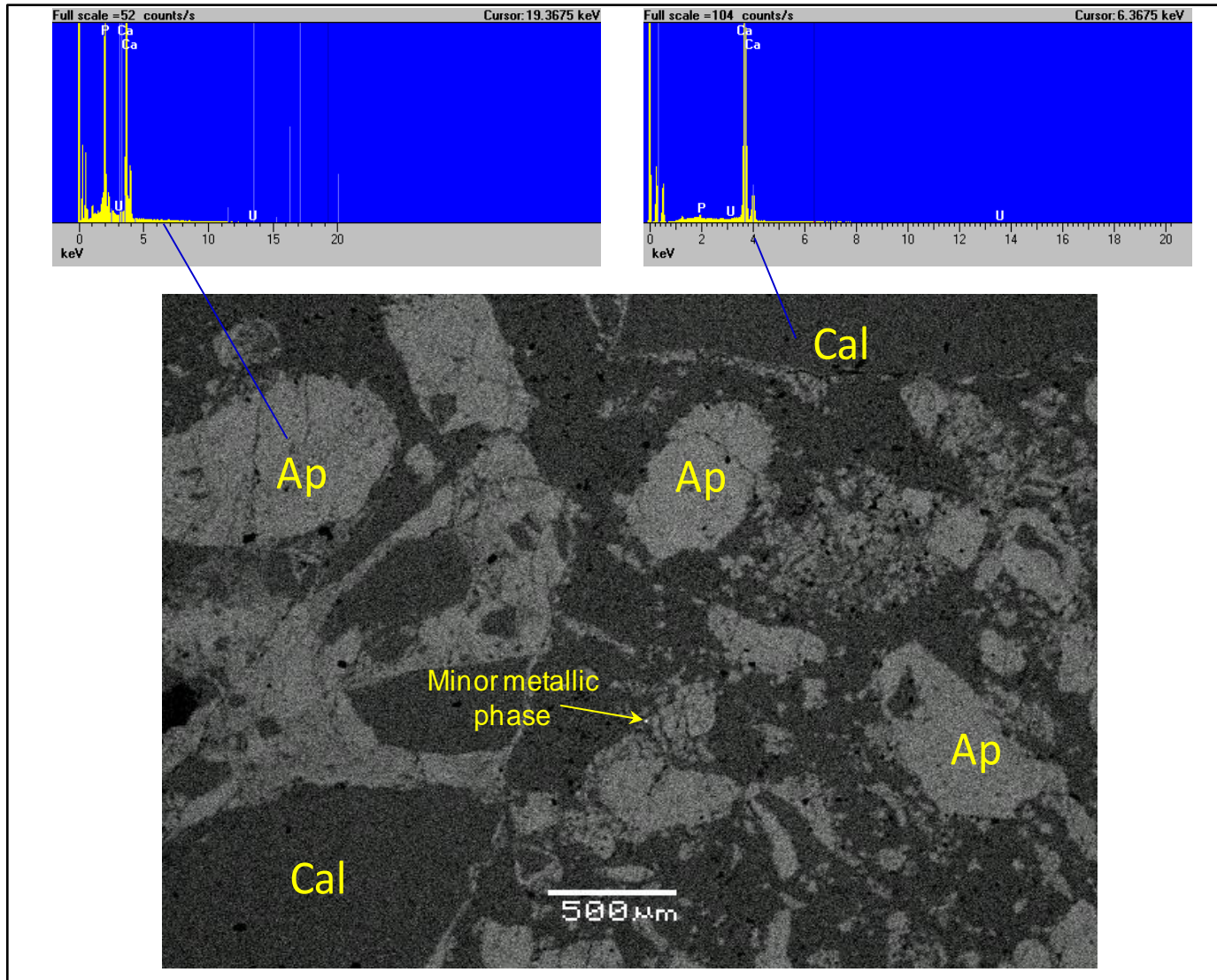
Sample: PER2



U-bearing material



Mineral-Chemistry of U in the sample PER2b (U: 648 ppm)



The chemical characterization of separated crystals was performed on a JEOL JXA-8230 Superprobe Electron Probe Microanalyzer at the Institute of Geosciences and Sciences of the Paulista State University (San Paulo, Brasil).

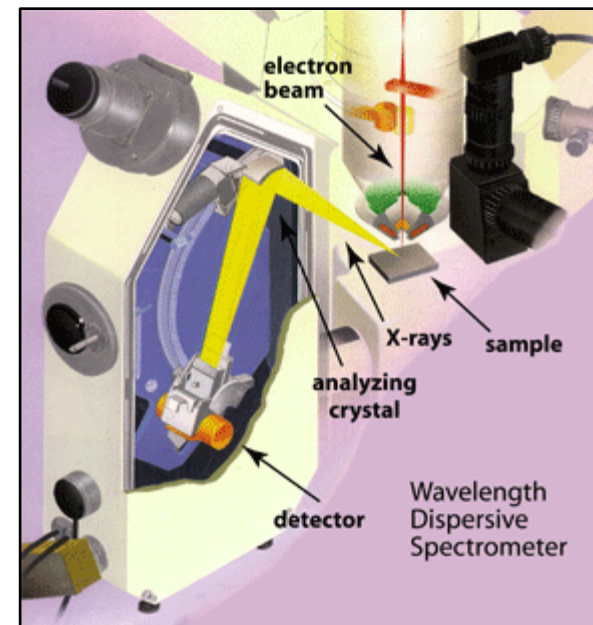
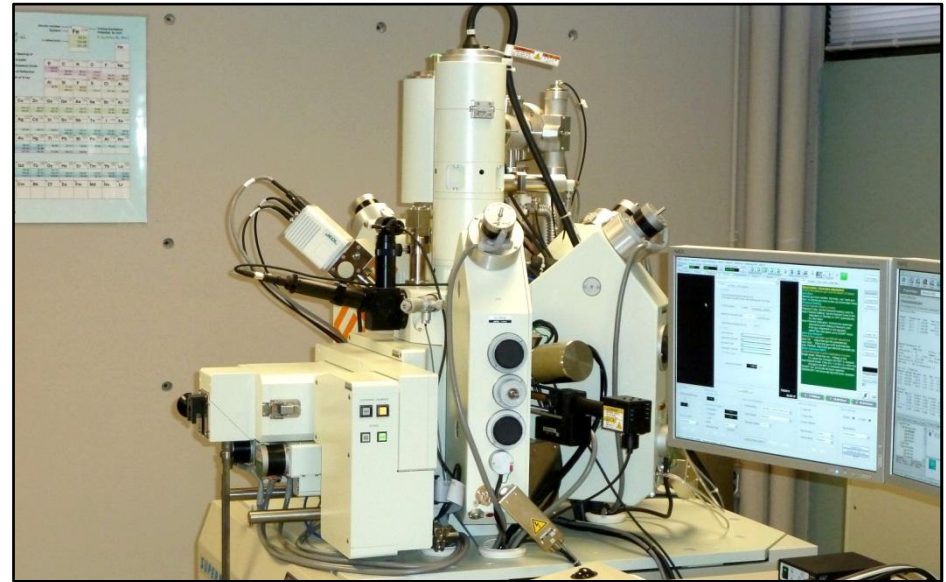
Energy Dispersive Spectra (EDS) were acquired with a silicon drift detector with energy resolution (FWHM) of 129 eV for Mn-K α , at 3000 cps.

Wavelength Dispersive Spectroscopy (WDS) scans were performed using using a number of diffracting crystals (LDE1, TAP, PETL and LIFH) each of them appropriate for the determination of the specific elements. The dwell time was 60 ms and the position steps 50 μm .

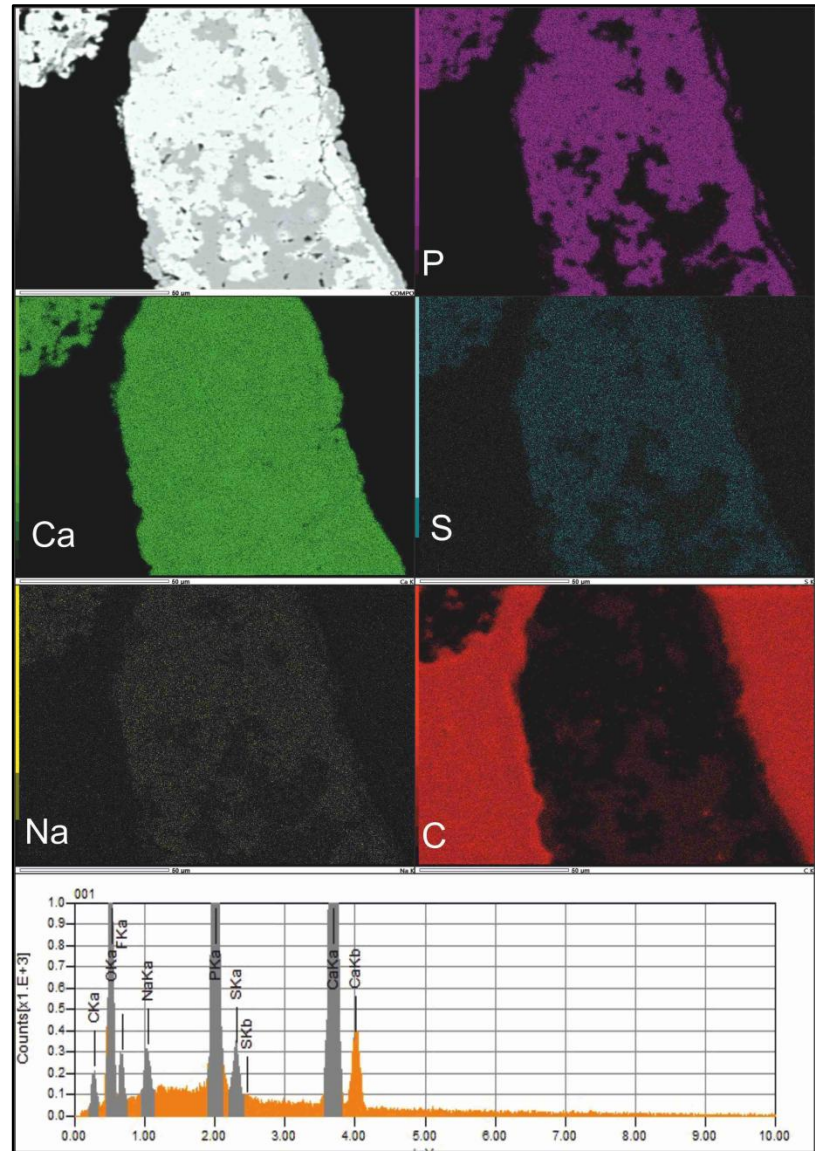
The standardization of the WDS was performed measuring the FK_{α} , CaK_{α} and PK_{α} in F-Apatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), SiK_{α} in wollastonite (CaSiO_3), UM_{α} in UO_2 , ClK_{α} in sodalite ($\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$) and SK_{α} in pyrite (FeS_2).

The acceleration voltage for the quantitative WDS analyses was kept at 15 nA in order to minimize deterioration or destruction of the crystals.

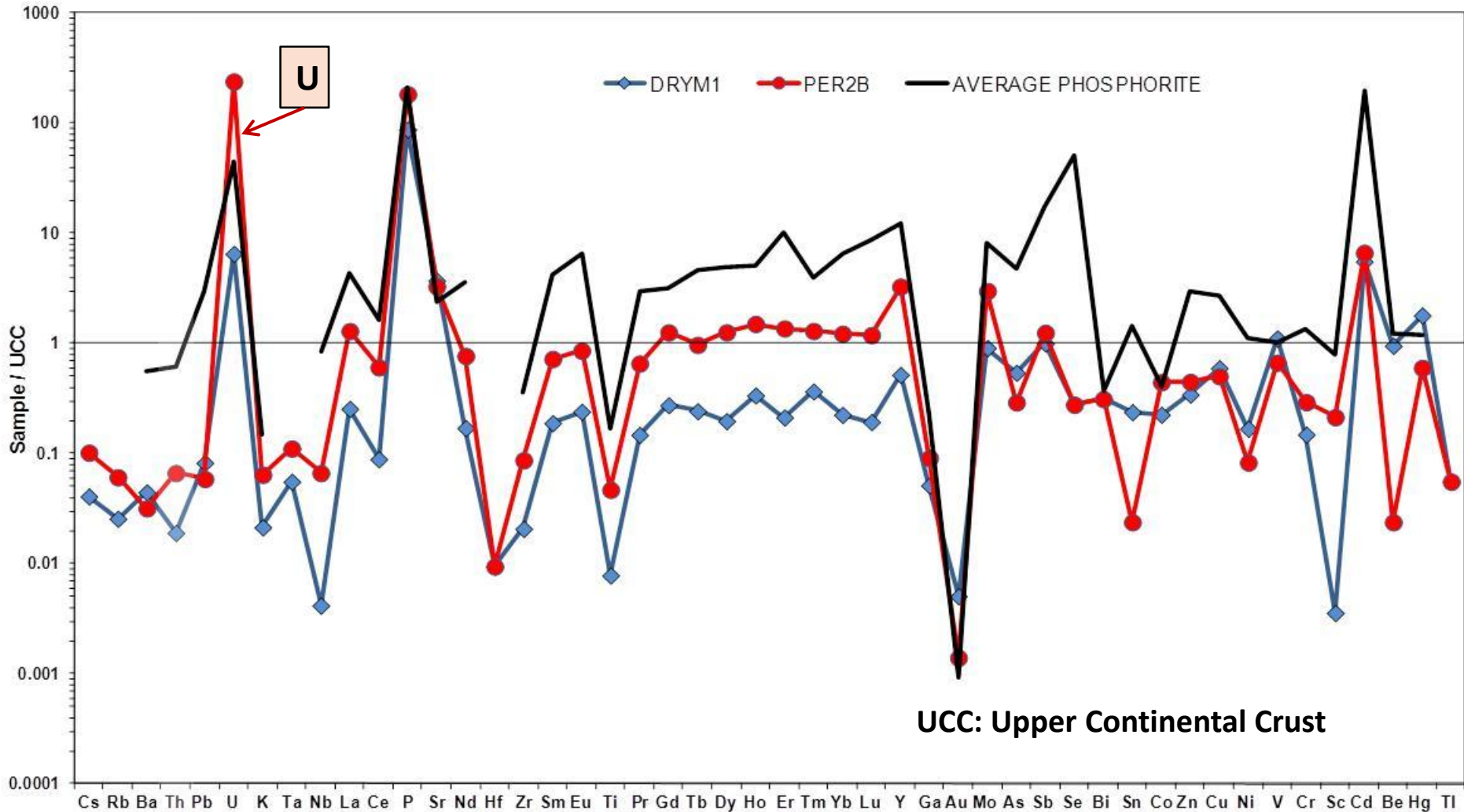
The beam diameter was 10 μm .



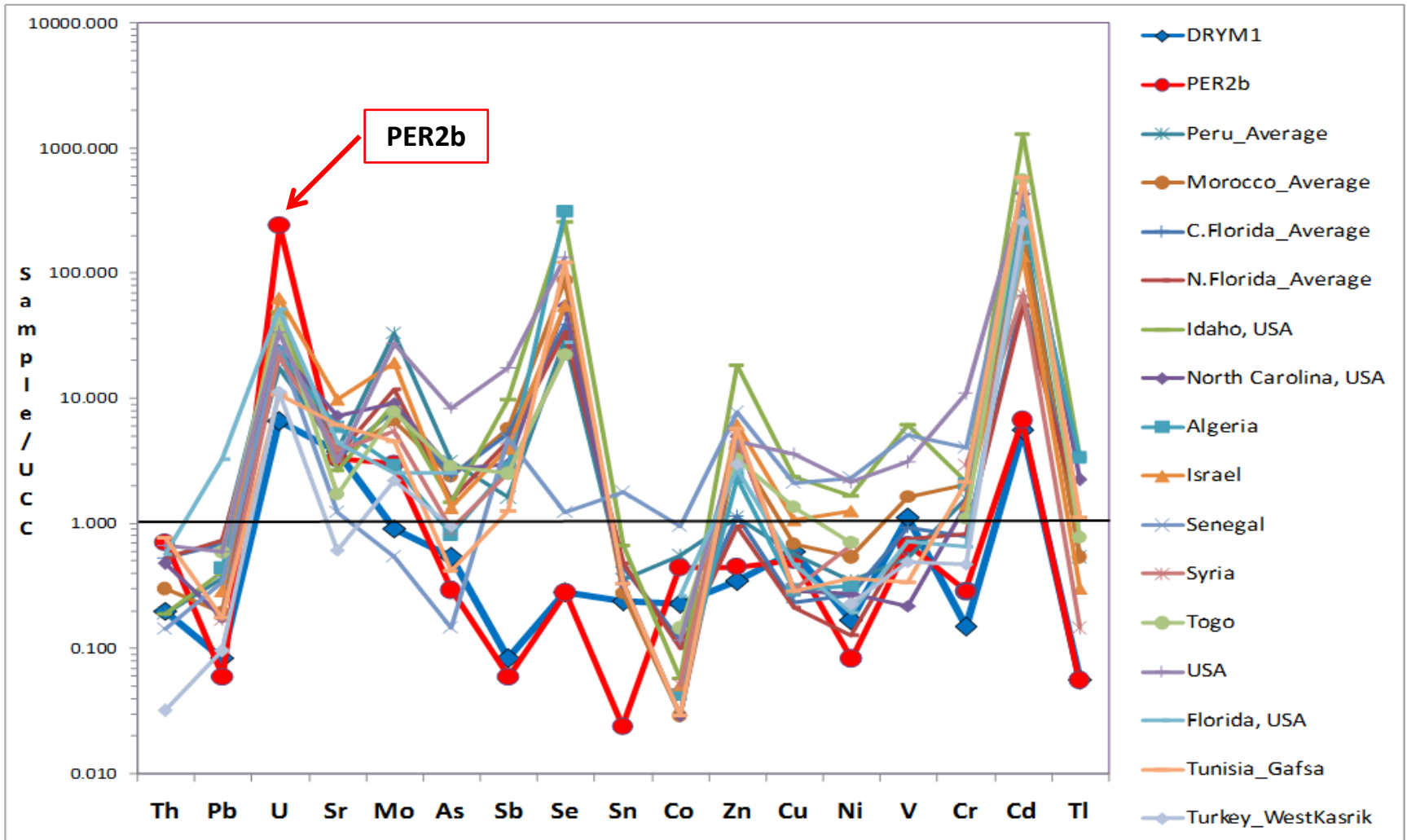
Microprobe elemental maps of a francolite crystal showed that the crystals were not homogeneous



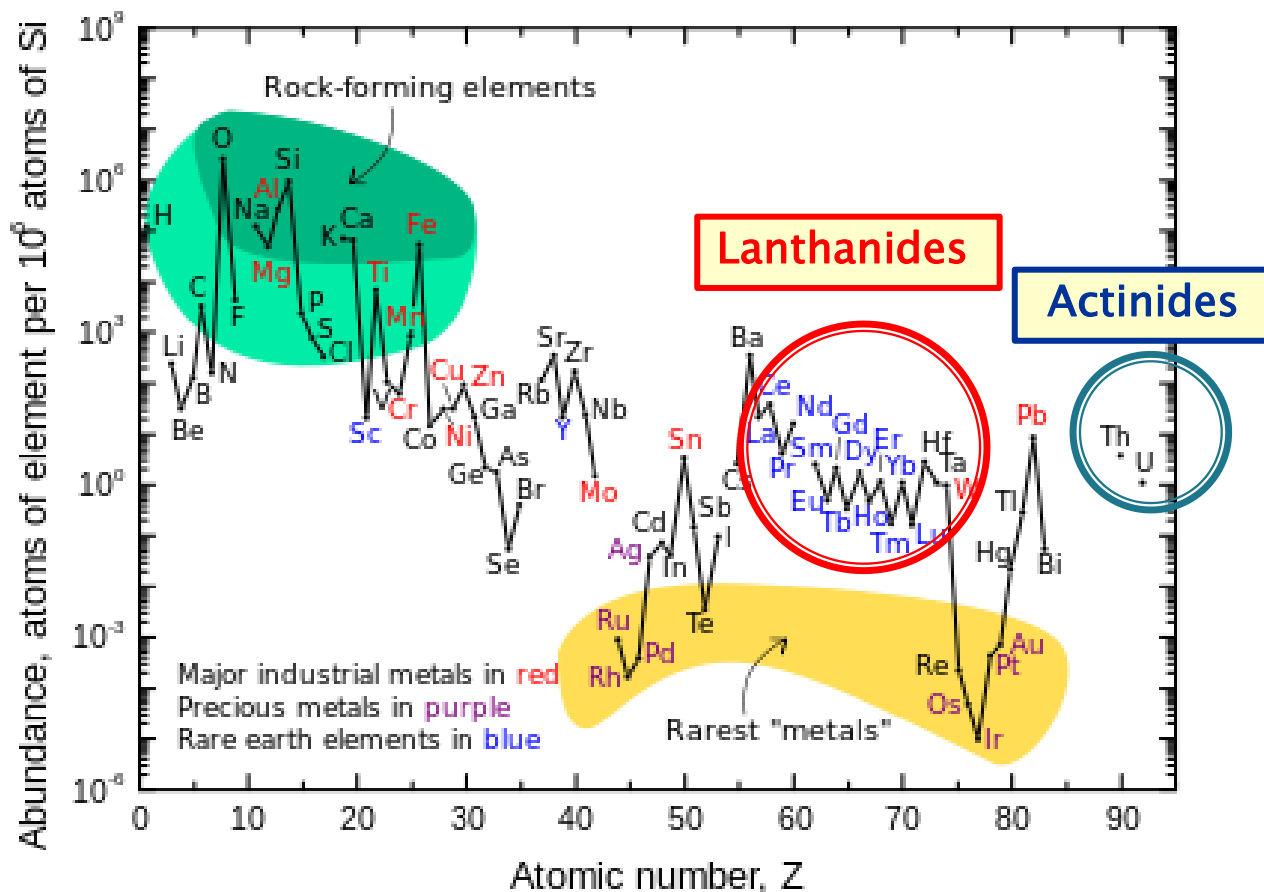
Element concentration in the studied Epirus mesozoic phosphorites compared with the global average.



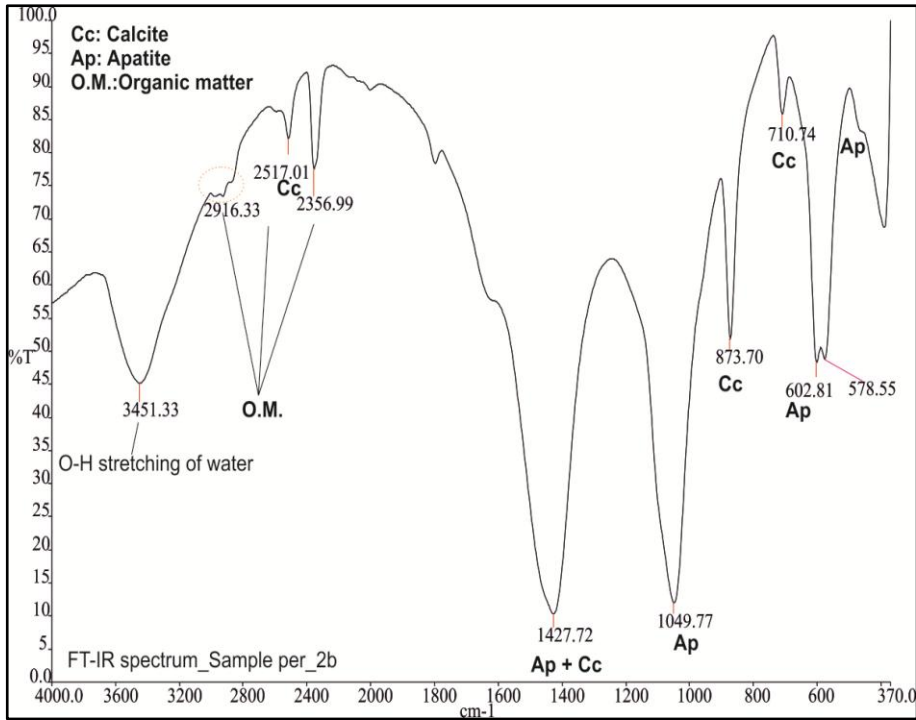
Epirus mesozoic phosphorites compared with world phosphorites



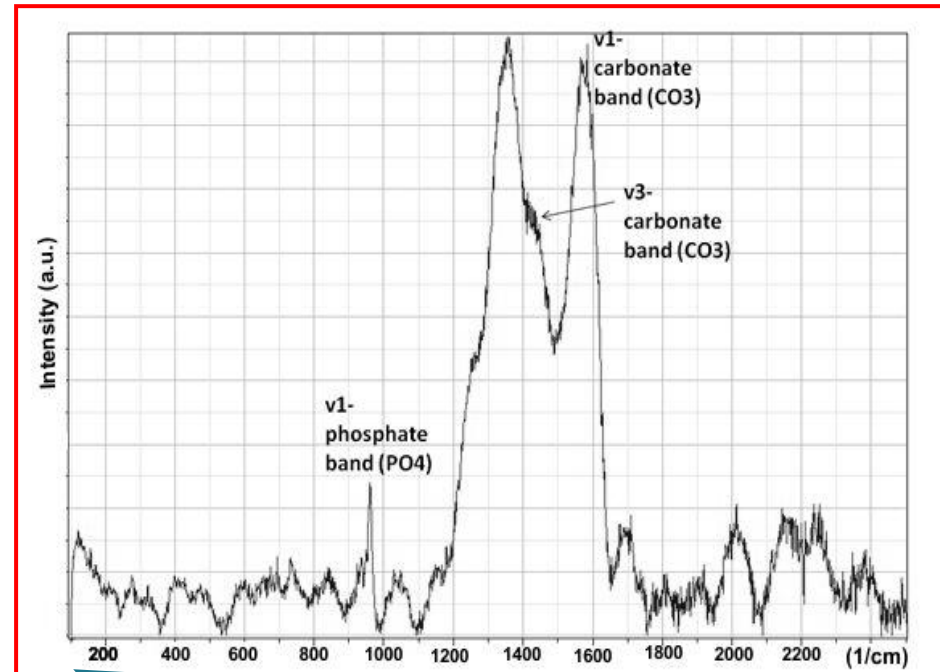
Abundance of Actinides and lanthanides in the Earth Crust



FT-IR Spectroscopy



Raman Spectroscopy



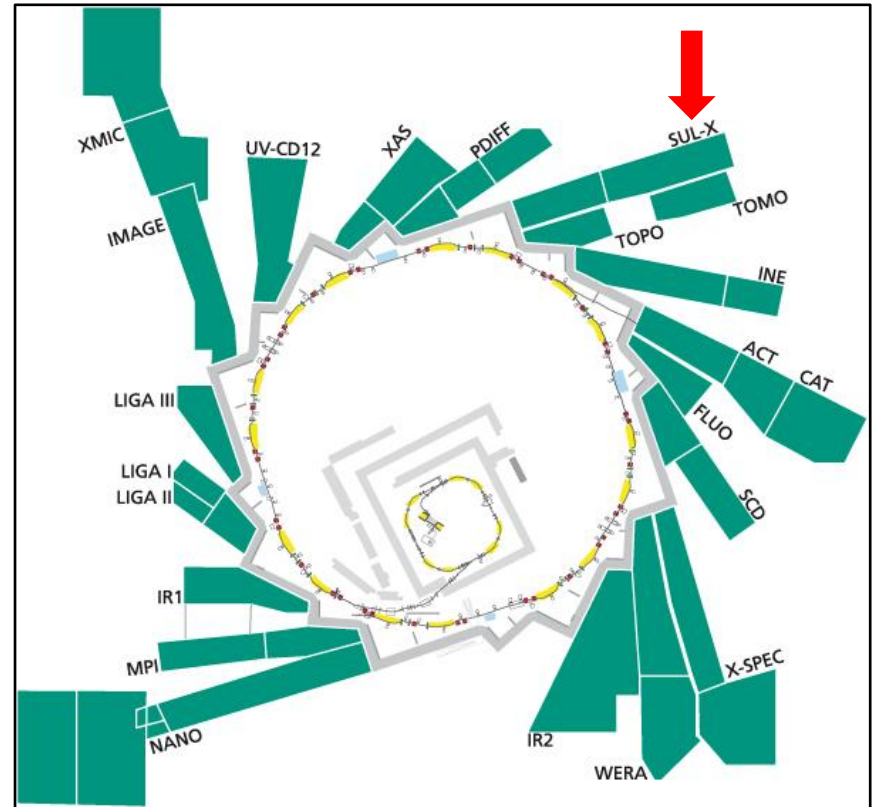
The separated carbonate apatites (francolites) had optically different appearance than the classical ones. They appeared as opaque crystals without a specific shape showing different shades of brown. They were identified by Raman spectroscopy combined with SEM/EDS microanalysis.

The Raman spectroscopy measurements were performed at the University of Heidelberg using a Horiba iHR320 Raman Spectrometer, equipped with a 532 nm Laser (green) and a Horiba Superhead as optional confocal optic.

Synchrotron Radiation Measurements

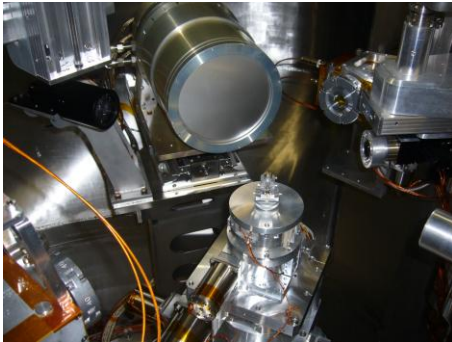
Synchrotron radiation (SR) micro-X-Ray Fluorescence (μ -XRF) and -X-Ray Absorption Near Edge Structure (μ -XANES) spectra were obtained using powders and polished sections in the SUL-X beamline of the Laboratory for Environmental Studies of the ANKA facility (Karlsruhe Institute of Technology, Germany). The sample area of the thin polished section of the phosphatized limestone to be analyzed by μ -XRF was selected using an optical microscope.

The intensities of the Ca, P, S, Y and U fluorescence emission lines excited by 17.5 keV X-rays were simultaneously determined by a 7-segment Si(Li) detector.

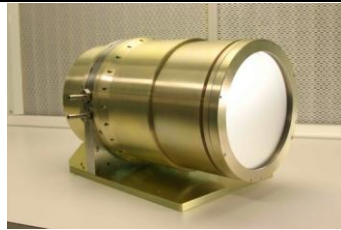
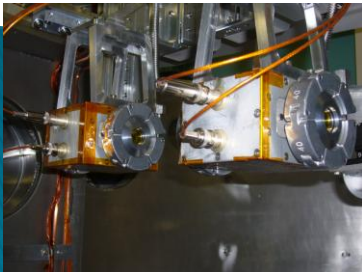


SR μ -XRF/ μ -XANES / μ -XRD (SUL-X beamline, ANKA Synchrotron, KIT)

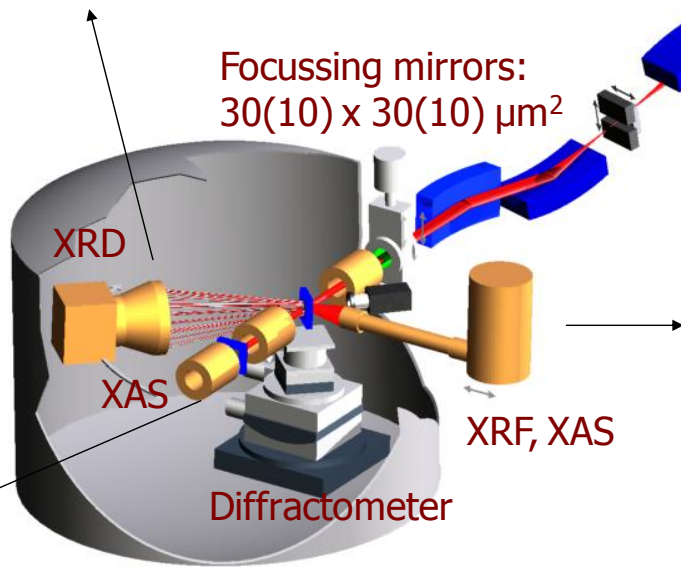
Inside the chamber:
Diffractometer and
detectors



μ -XANES/EXAFS:
Ionization chambers



μ -X-ray diffraction:
CCD detector



Vacuum chamber

Brilliant X-ray
source: Wigner

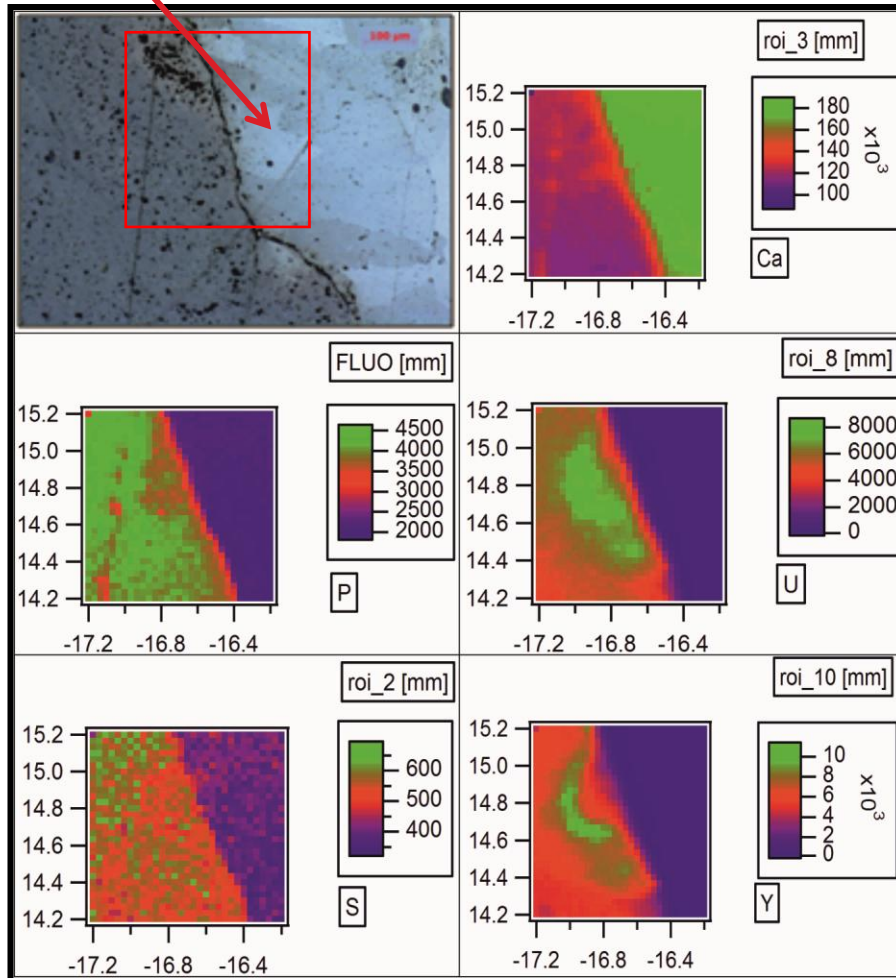
Monochromator
2.4 (1.4) - 21 keV

μ -X-ray fluorescence
spectroscopy:
7 element Si(Li) detector)



SR μ -XRF elemental maps

Calcite

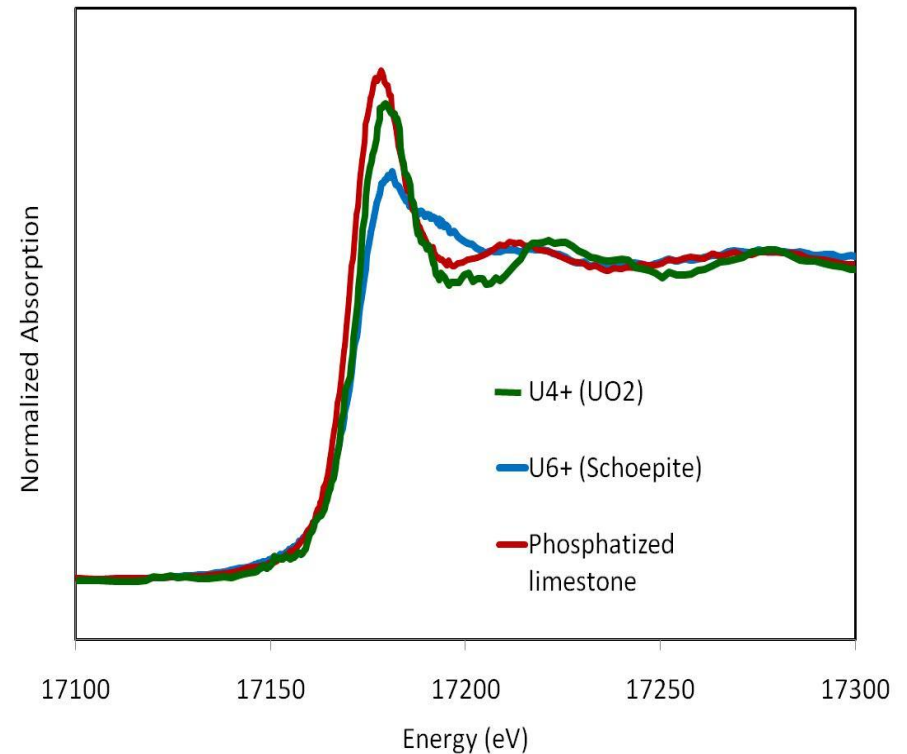


The combination of the SR μ -XRF maps of the bulk rock with those of the francolites carried out by SEM/EDS leads to the conclusion that the uranium is concentrated in the organic rich part of the phosphatized limestones and more specifically in the francolites. The positive correlation between uranium and phosphor additionally strengthens this conclusion.

Optical image of the polished section of the U-bearing limestone (upper left) and qualitative SR μ -XRF elemental maps. The dark side corresponds to the organic-rich component, where U (and P) is mostly accumulated, while the bright one to Ca-carbonate.

UL_3 -edge μ -XANES spectra

On areas with elevated uranium concentration μ -XANES data were recorded at the UL_3 -edge (about 17.170 keV). The powdered samples measured as pellets were prepared by mixing the sample with a binding agent (cellulose). Uraninite (UO_2) and schoepite ($UO_2(OH)_2$) were used as reference materials for uranium.



Uranium seems to appear in the oxidation state 4+.

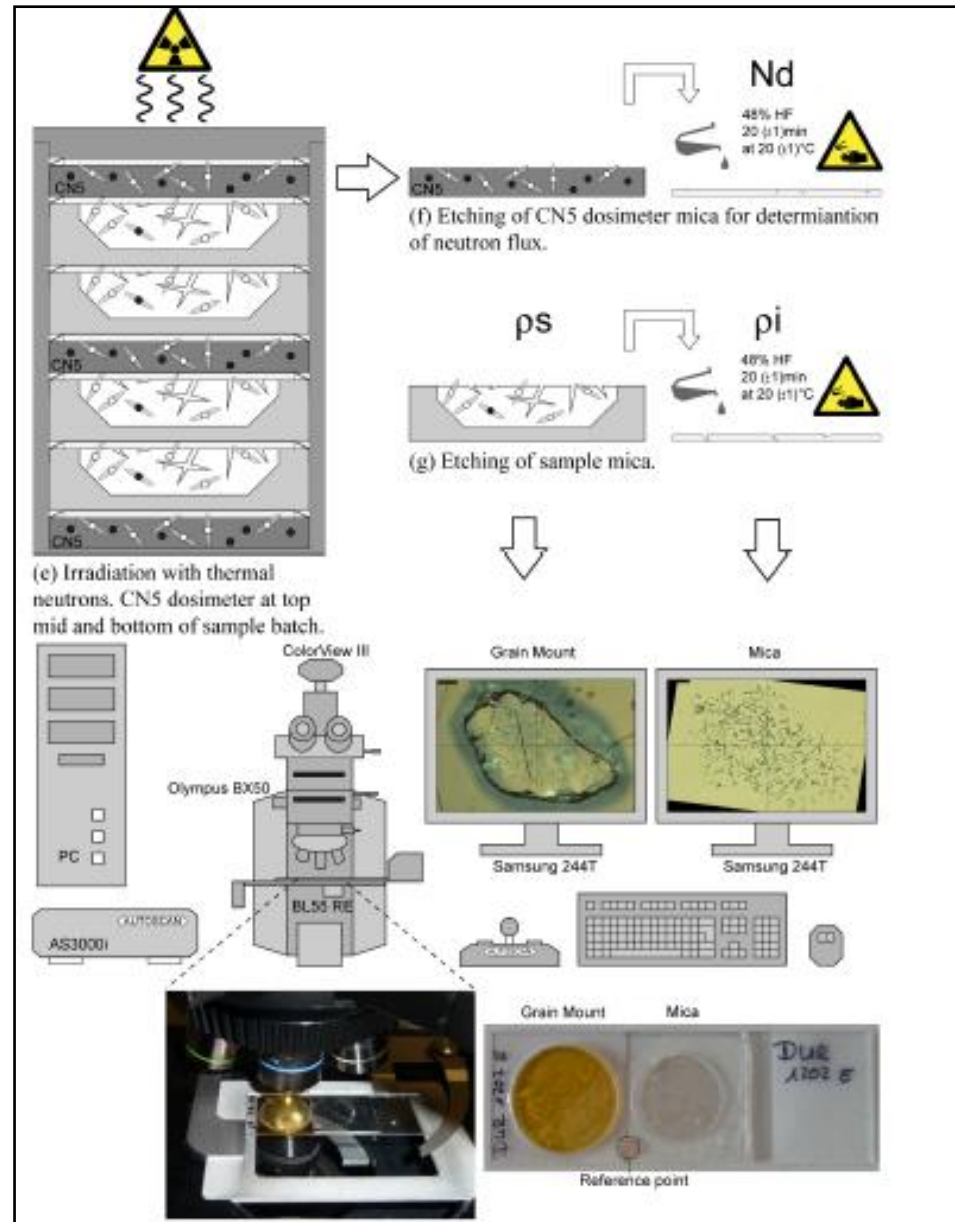
The oxidation state determination contributes to a better understanding of the geochemistry and migration/immobilization of uranium into the geological environment and additionally to the elucidation of the redox phenomena taking place.

Fission track measurements

The presence of uranium in the francolite crystals was additionally evidenced by fission track measurements. Enhanced number of fission tracks were revealed in the U-free mica foils attached to embedded, polished and cut francolite crystal samples after neutron irradiation and etching.

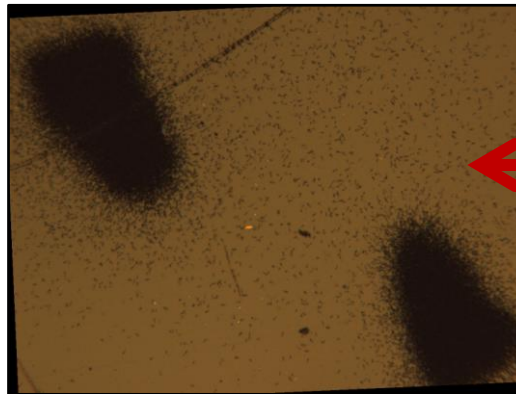
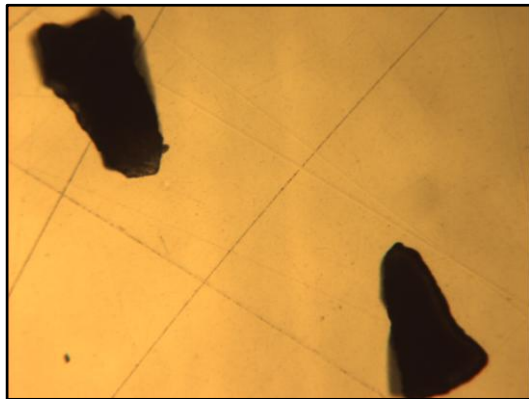
The samples, along with CN5 dosimeter glasses, were irradiated with neutrons at the FRM II high flux research reactor of the Technical University of Munich at Garching.

After the irradiation and decay of the induced radioactivity, the mica foils were etched for 20 min by 48% HF in ambient temperature (20°C) and the fission tracks then visualized by optical microscopy.

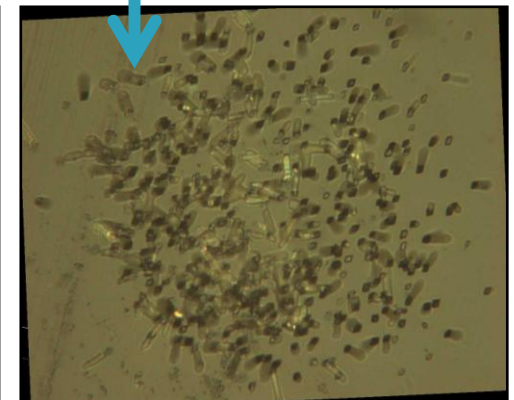
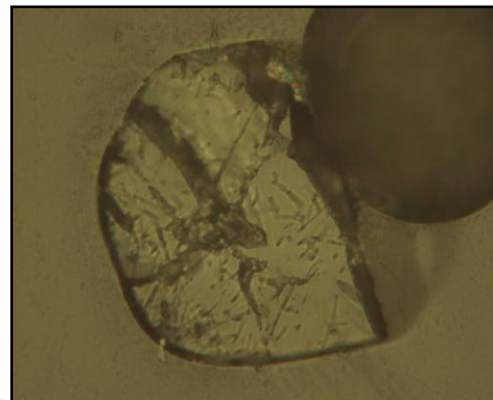


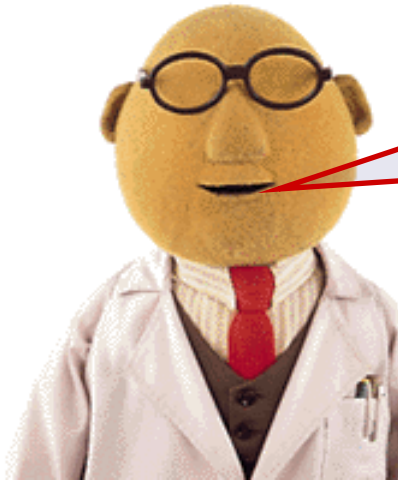
Fission track measurements

The number of fission tracks originating from the francolite crystals could not be quantified because of their enhanced uranium content. **This finding, confirming the uranium presence in sedimentary francolite crystals, has not been, to our knowledge, previously reported in the literature.**



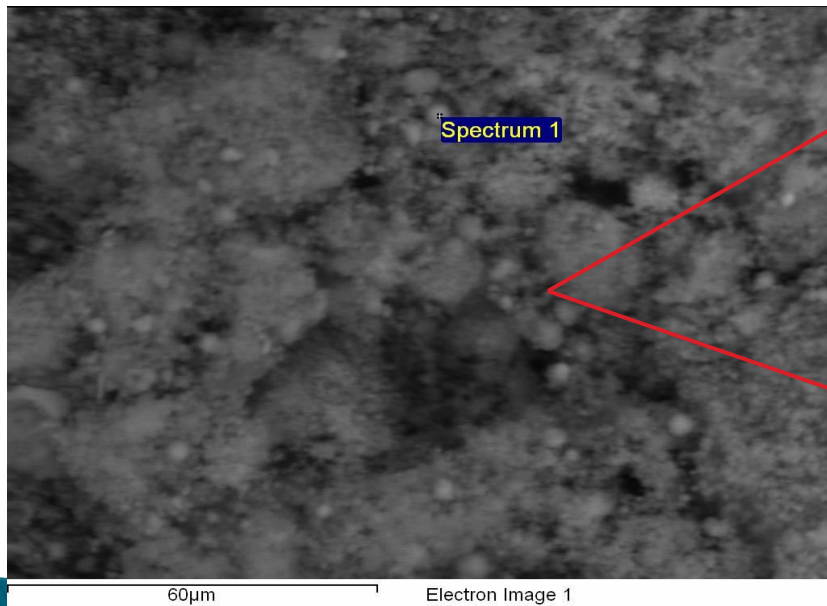
Fission tracks from
Francolite
Fluorapatite



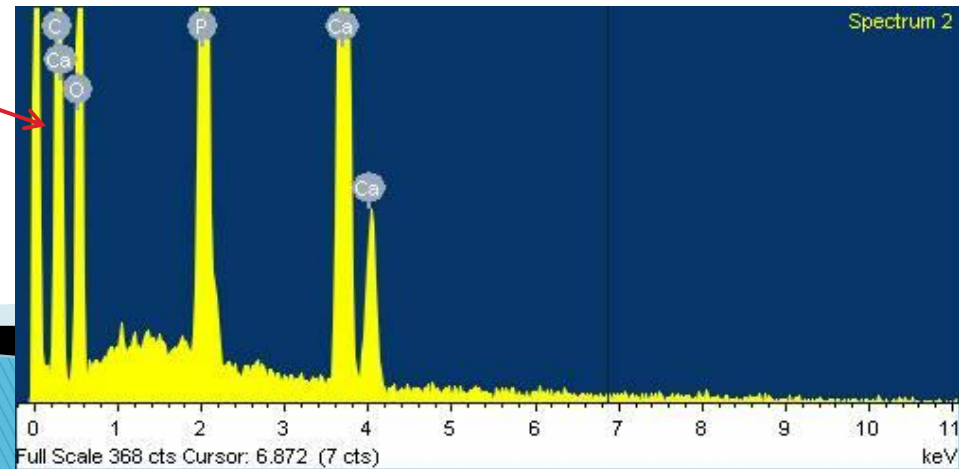
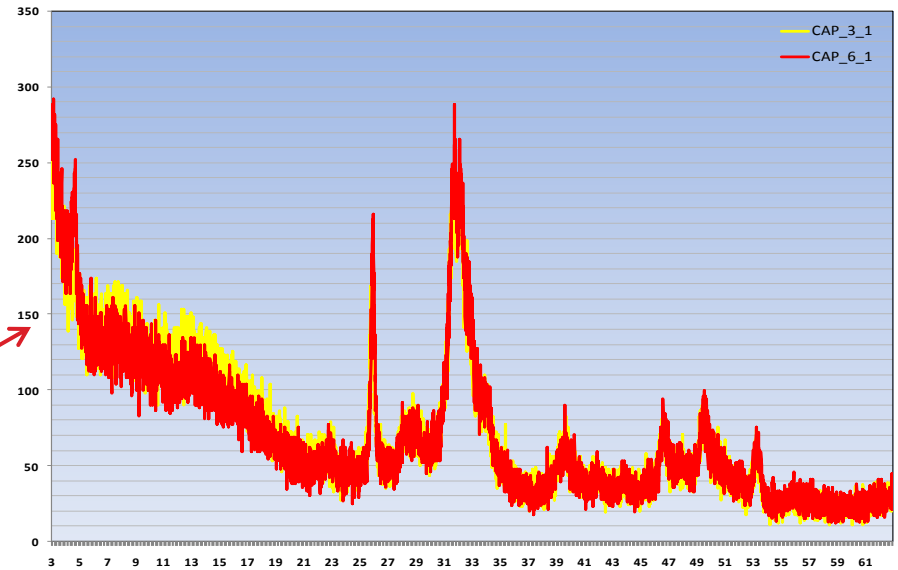


A few words about the work being in progress

Interaction between U and synthesized carbonate apatites



Spectrum 1

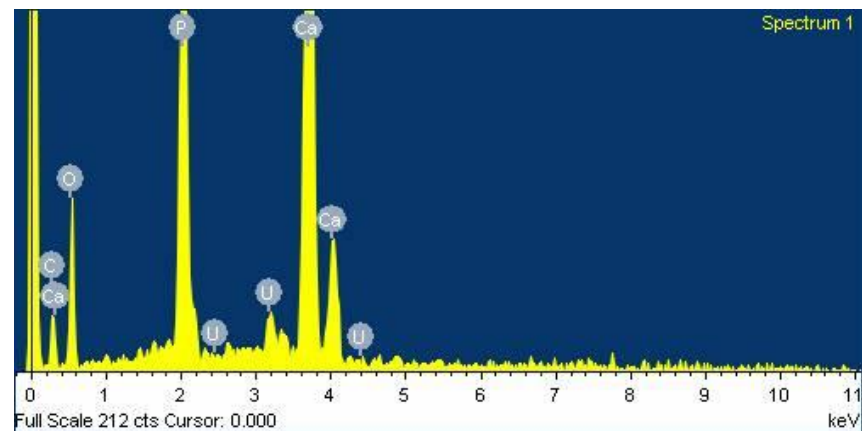


BSE image, XRD pattern
and EDS of synthesized carbonate apatite

U-sorption tests using synthesized carbonate apatites



Electron Image 1



Element	Weight%	Atomic%	Compd%	Formula
P K	19.55	15.52	44.79	P_2O_5
Ca K	35.77	21.95	50.05	CaO
U M	4.29	0.44	5.16	UO_3
O	40.39	62.08		
Totals	100			

Semi-quantitative analysis of synthesized carbonate apatites from SEM-EDS after U sorption tests

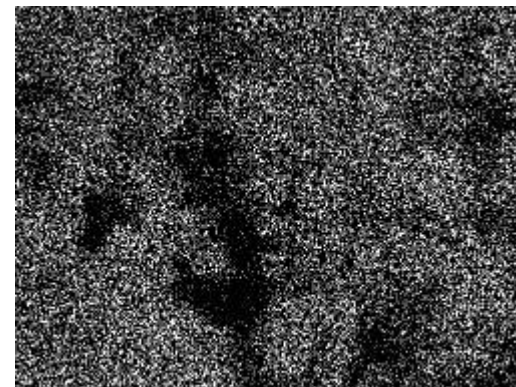
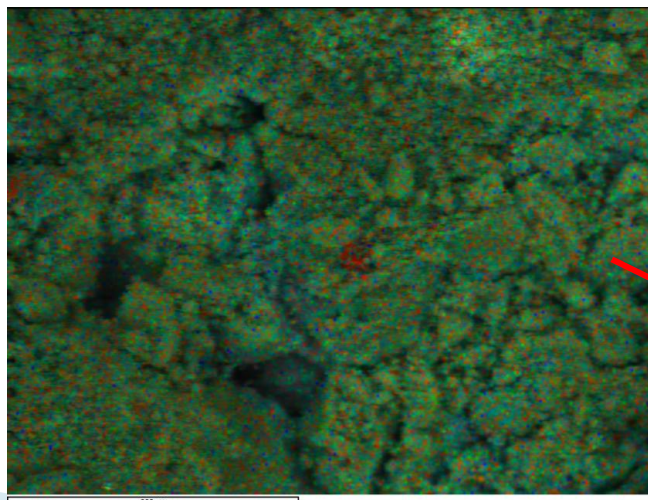
Element mapping on the synthesized carbonate apatite using SEM-EDS

BSE initial photo

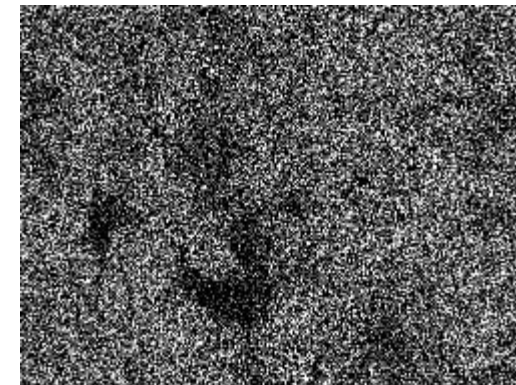


Electron Image 1

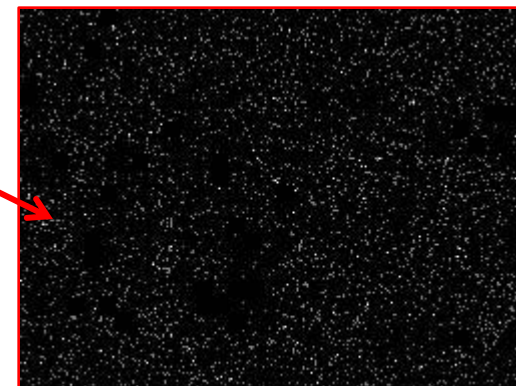
BSE U-mapping
(red color)



P Ka1

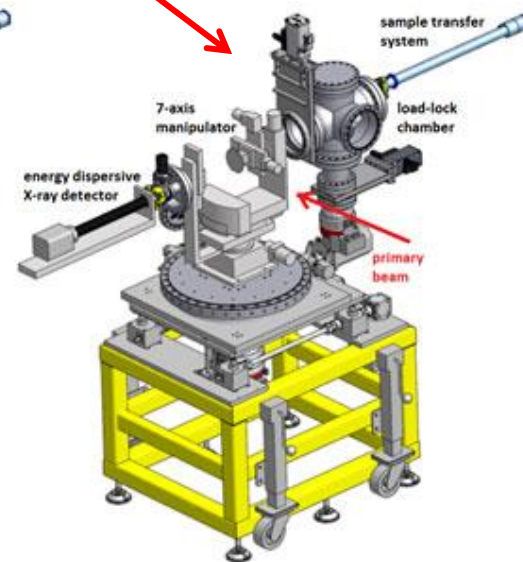
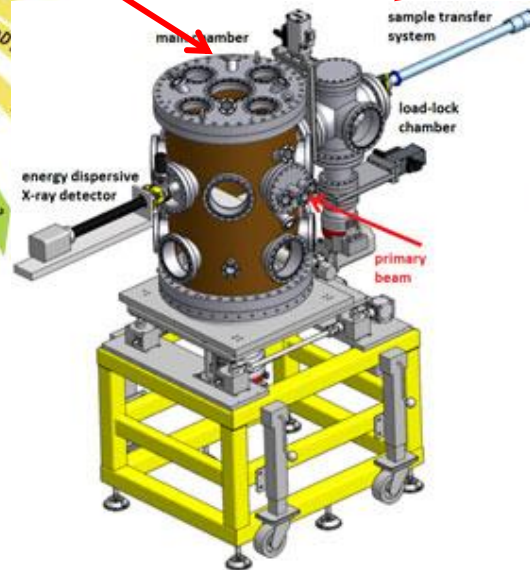
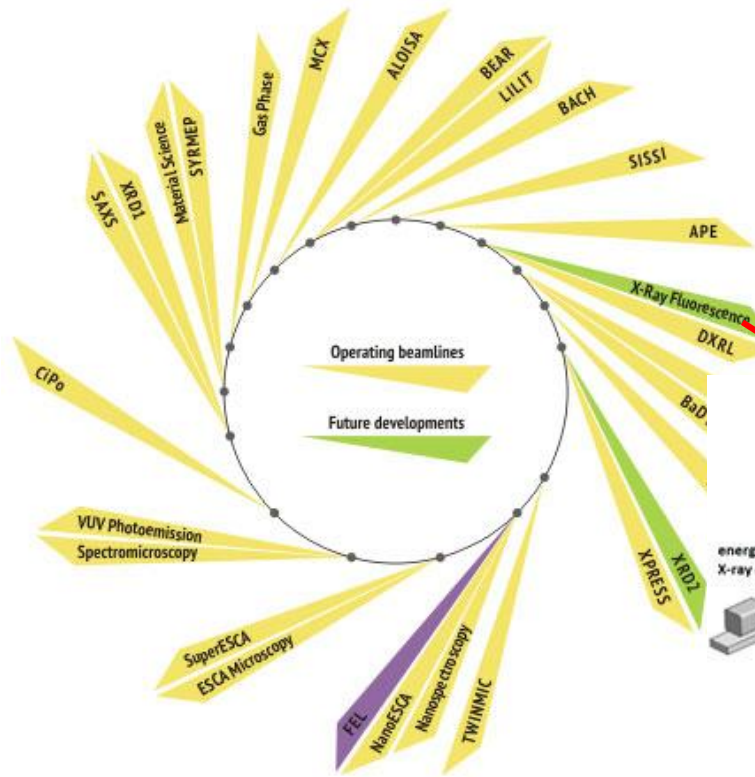
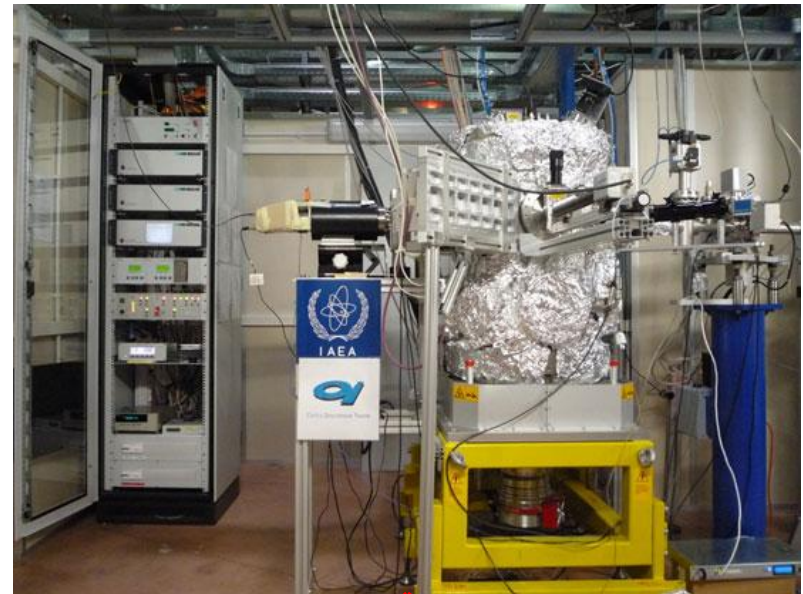


Ca Ka1



U Ma1

Presence of uranium in francolite crystals was also observed in recent experiment at the XRF-Beamline of the Elettra Synchrotron (Trieste) using the U-M_{IV} X-rays.

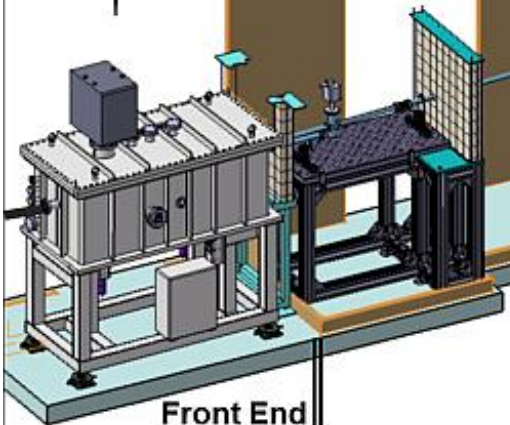


Synchrotron X-Ray Beam



Collimation Mirror
Monochromator
Refocusing Mirror

Shutter



Front End

S.S.1



Pumping Station

Higher Order Suppressor

S.S.2

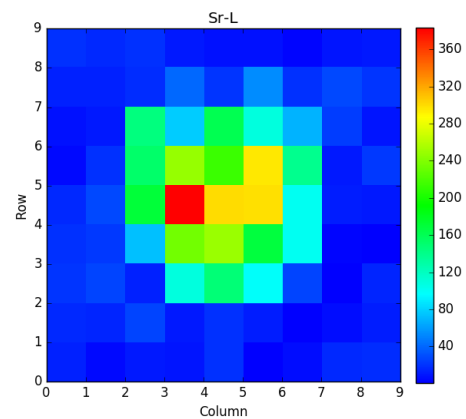
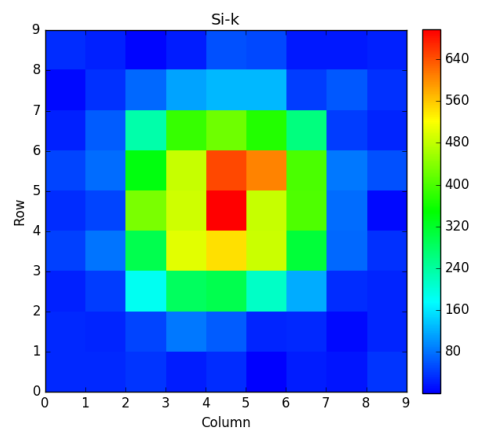
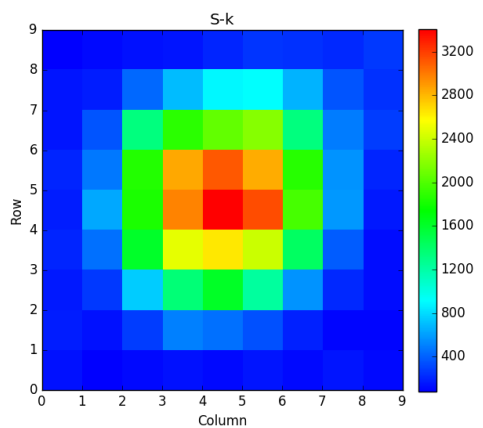
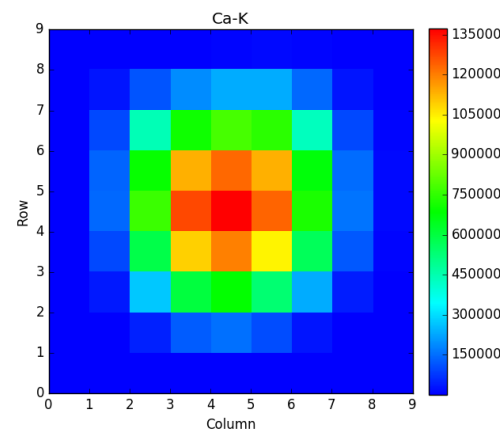
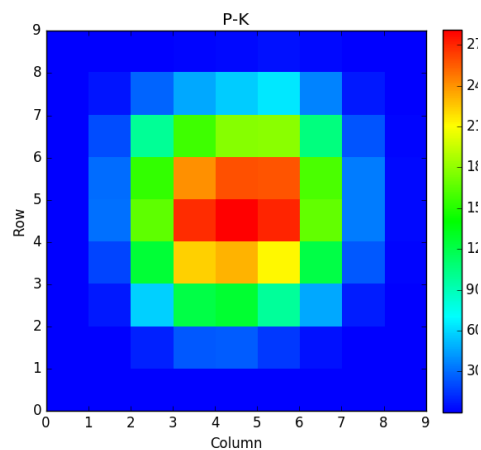
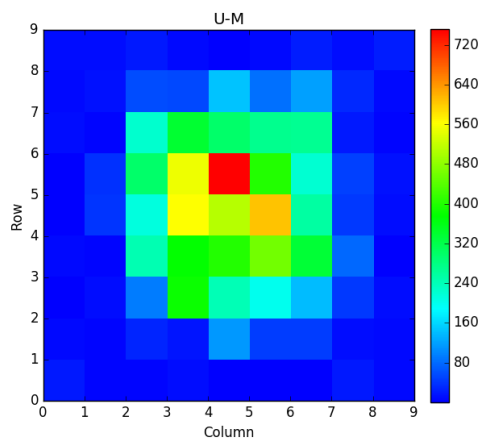
Filters

Exit Slits

UHVC End Station



Raw μ -XRF data from the study of a francolite crystal obtained during recent experiment at the Elettra Synchrotron (Trieste)



Summary

The organic rich limestones from NW Greece (Epirus region) were found to exhibit radioactivity due to presence of uranium.

Organic matter, apatites, francolites (carbonate apatites) and calcite were the main phases of the rock identified.

μ -XRF elemental mappings applied to polished thin section of the sample showed that the uranium exclusively existed in the organic rich part of the sample also containing apatites and francolites.

The francolites were identified by combining microprobe data with Raman spectroscopy.

The density of homogeneously distributed fission tracks highlighted the enhanced U-content of francolites.

μ -XANES study revealed that the uranium existed in the U^{4+} oxidation state.

Furthermore, the fission track results showed that francolites could be a perfect candidate for thermochronology dating due to their high U content.

THE ORIGIN OF URANIUM REMAINS STILL A NOT-ANSWERED QUESTION REQUIRING FURTHER INVESTIGATION.

Part of these data has appeared in the literature as:

Tzifas, I.T., et al., Uranium-bearing francolites present in organic-rich limestones of NW Greece: a preliminary study using synchrotron radiation and fission track techniques. J Radioanal Nucl Chem 311 (2017) 465.

The evaluation of the rest material is still in progress.

Previous publication on this subject:

Tzifas, I. T., et al., "Uranium-bearing phosphatized limestones of NW Greece." *Journal of Geochemical Exploration* 143 (2014) 62-73.

The authors would like to thank

Prof. U.A. Glasmacher and Mrs. M. Brückner (Thermochronology and Archaeometry Group, Inst. of Earth Sciences, Univ. of Heidelberg, Germany),
Assoc. Prof. A. Godelitsas (Dept. of Geology & Geoenvironment, University of Athens, Greece),

Drs. J. Goettlicher and R. Steininger (ANKA Synchrotron Radiation Facility, Karlsruhe Institute of Technology, Germany),

Dr. D. Françoso de Godoy (Depto. de Petrologia e Metalogenia, Univ. Estadual Paulista, Brasil) and

Dr. A. Karydas (NCSR Demokritos, Athens, Greece)

for their support, assistance and advise.

The support of DAAD to this work is also thankfully acknowledged.

*Thank you very much
for your attention!*

