Potential for Fractured Higher Strength Rocks to Uptake Radionuclides from Groundwater – A Natural Analogue Study

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Introduction

- Background/Issues
- Purpose of study
- Sample selection / samples
- Analytical techniques
- Initial results
- Preliminary conclusions / outstanding questions
- Next steps

Background

- Fractured higher strength rocks (HSR) are one of the rock groups that may provide a suitable low-permeability host for a Geological Disposal Facility (GDF) for radioactive wastes in the U.K.
- Radionuclide retardation within HSR may be important in the safety case for a HSR-hosted GDF

Important Issues

- Radionuclide retardation in rock matrix requires:
  - radionuclide transfer into the matrix from water moving in fractures by:
    - advection and diffusion
    - a variety of possible pathways
  - mechanisms by which radionuclides can be incorporated into the rock mass:
    - adsorption to existing grain surfaces
    - diffusion into grain interiors
    - incorporation into new minerals
- Radionuclide uptake/retardation mechanisms have been studied extensively, both in-situ and off-site, but studies address:
  - timescales several orders of magnitude shorter than duration of transport/retardation processes that need to be considered in a safety case
  - correspondingly shorter length scales than are relevant to the safety case

Purpose

- To *complement* experimental studies, RWM is undertaking a natural analogue study of transport/ retardation of radionuclides, and chemical analogues for radionuclides, within HSR, to gain insights into
  - natural processes occurring over longer timescales than lab / in-situ experiments
  - natural processes in the absence of disturbance that accompanies lab / in-situ experiments
- Aim to develop an improved conceptual model for radionuclide transport and uptake over timescales comparable with those considered by safety assessments by:
  - interpreting observed natural variations in distributions / behaviours of radionuclides and their analogues
  - *together with* published results from lab / in-situ experiments
- The project commenced in September 2016 and will continue until the end of March 2018
- Here we present interim results

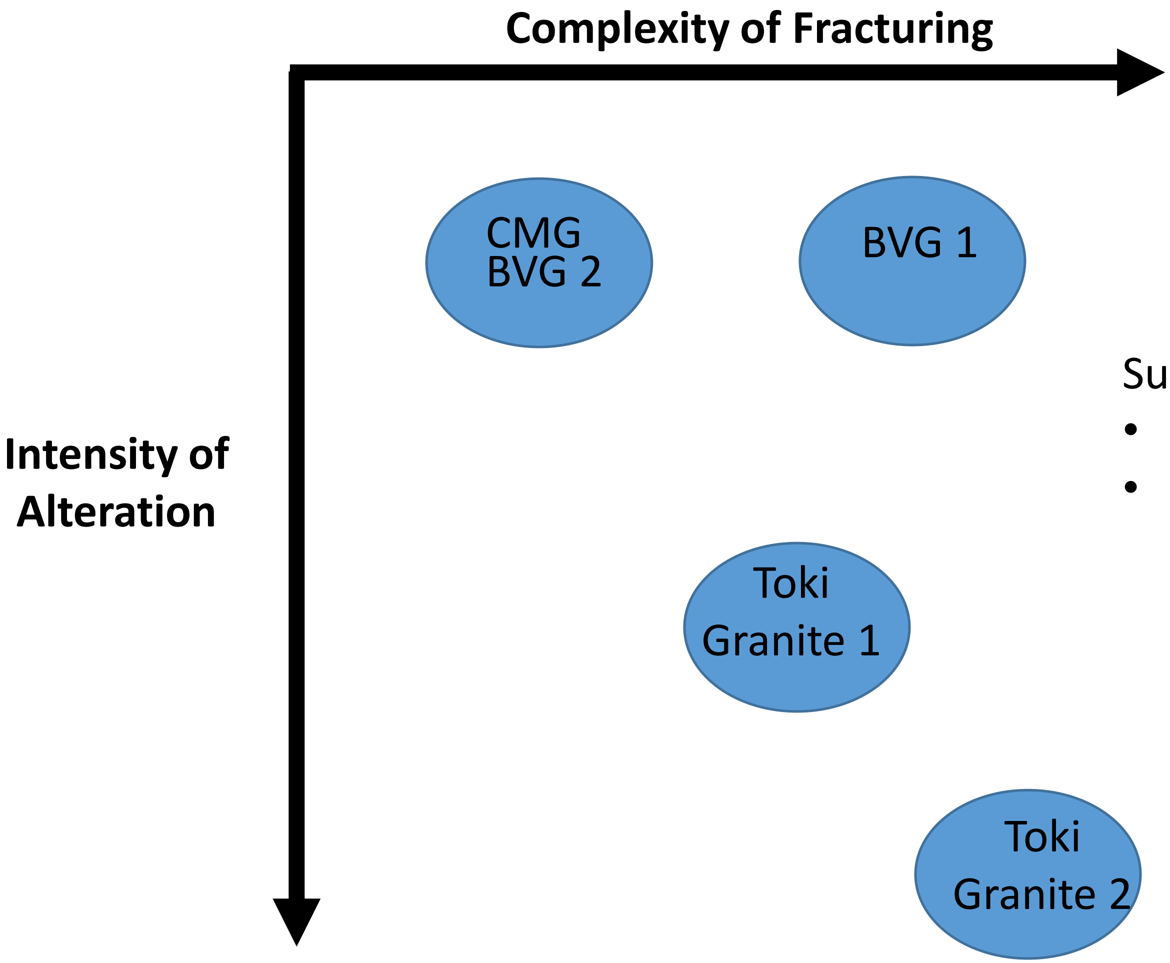
Sample Selection Approach

- A range of HSR types, with varied grain sizes needed
- Samples sufficiently large to enable various kinds of analyses
- Samples required to contain fracturing with different characteristics
  - complexity
  - geometries
  - associated mineral infills
  - wallrock alteration
- Samples required to contain fractures that have conducted water with P-T-chemistry similar those in plausible GDF host rocks
- Ideally corresponding groundwater chemical data

Selected Samples

- 2 fine-grained, Ordovician Borrowdale Volcanic Group (BVG) meta-tuff, NW England:
  - one has complex vein, associated fracture zone c. 30 mm across, v. little wall-rock alteration
  - one has hairline fracture, partly-sealed by v. thin calcite layer, network of fine anastomosing calcite-mineralised microfractures in wallrock, extend c. 5 mm, v. little wallrock alteration
- 1 medium grained, Permian Carnmenellis Granite, SW England
  - planar fracture thinly coated in laumontite and calcite with very limited associated microfracturing within the adjacent wallrock
- 2 medium grained, Cretaceous Toki Granite, central Japan:
  - MIU-3/8, moderate alteration, one major fracture bordered by fracture zone c. 5mm thick
  - MIU3/10, much more intensely altered with more complex fracture zone c. 20 mm thick, associated with an extensive microfracture network in the adjacent wallrock

Selected Samples



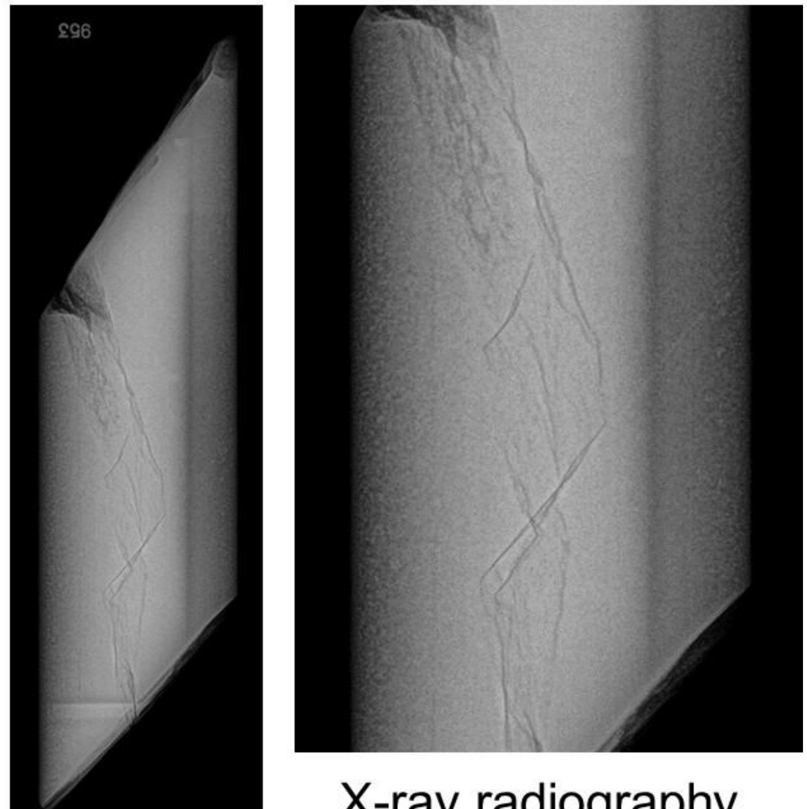
Suite of samples have:

- Range of fracturing complexity
- Range of alteration

BVG 1, Sellafield, NW England

BVG: Sellafield, SSK70953 (RCM3)

Core photography



X-ray radiography

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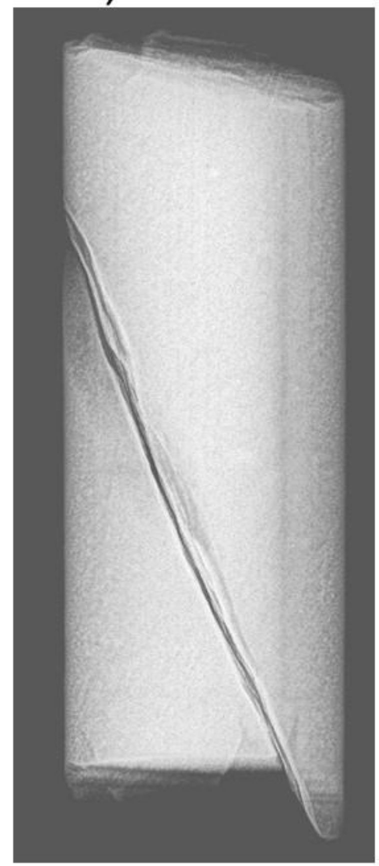
BVG 2, Sellafield, NW England

BVG: Sellafield, SSK70955 (BH9A)

Core photography



X-ray radiography

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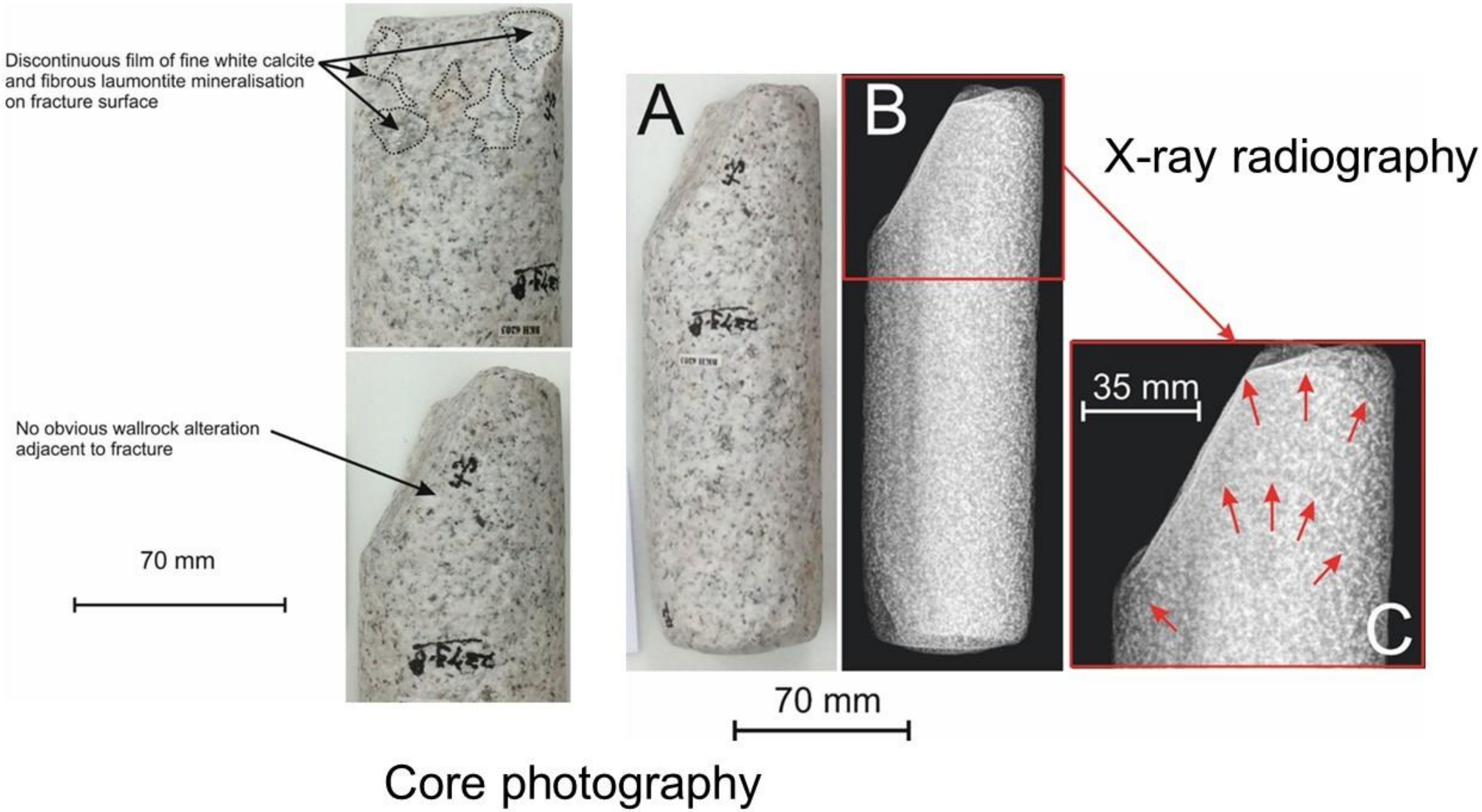
Carnmenellis Granite, SW England

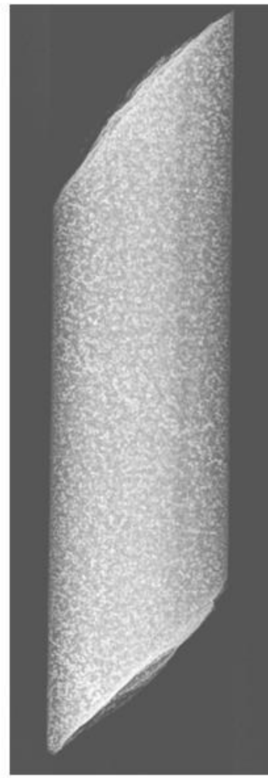
Carnmenellis Granite: Rosemanowes BH15: sample SSK70952

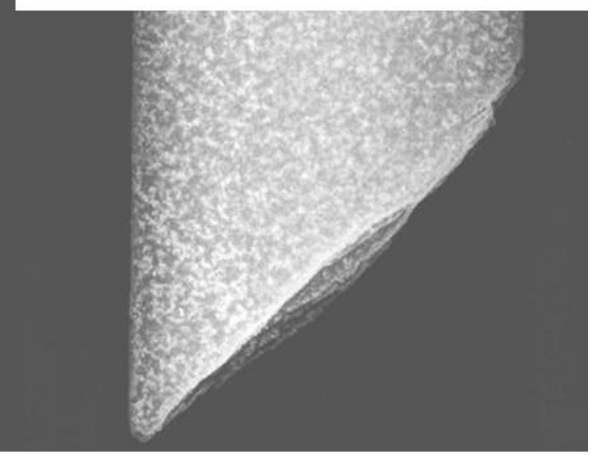


Toki Granite 1, Central Japan

Toki Granite: Mizunami, sample MIU-3/8

Core photography





X-ray radiography

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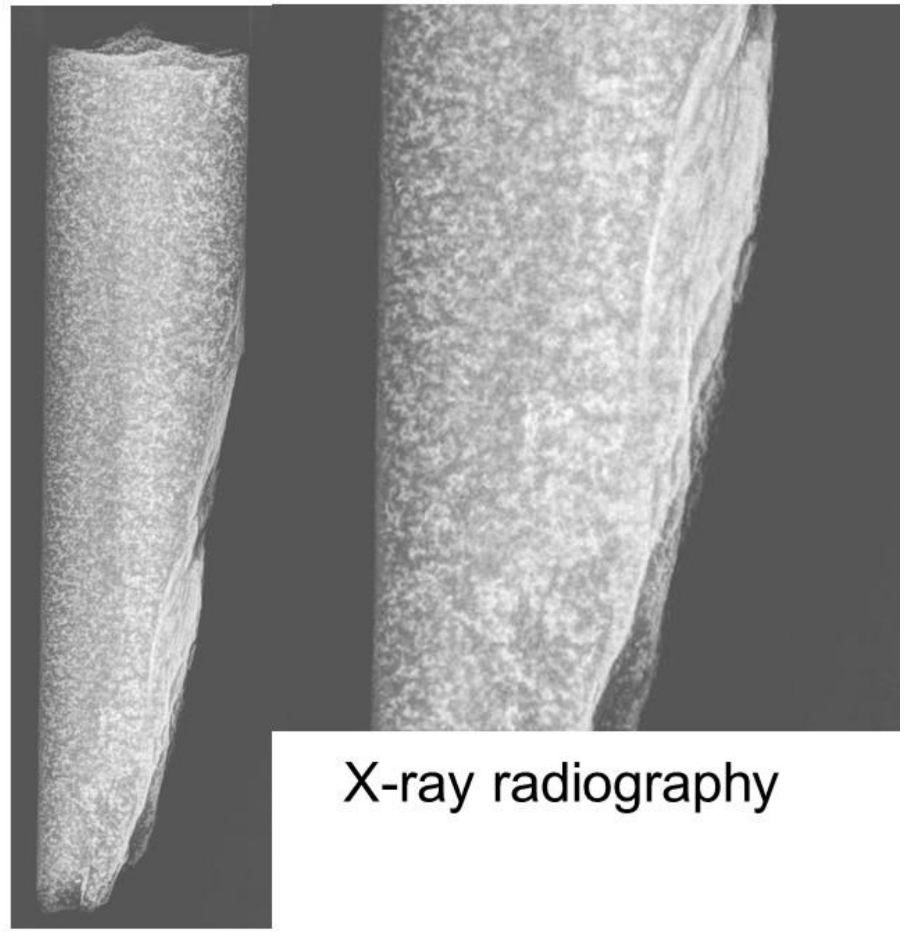
Toki Granite 2, Central Japan

Toki Granite: Mizunami, sample MIU-3/10

Core photography



X-ray radiography

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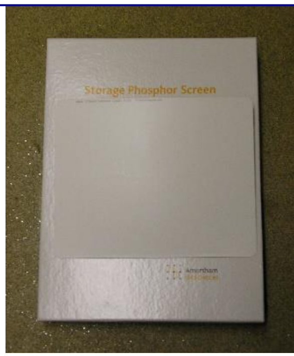
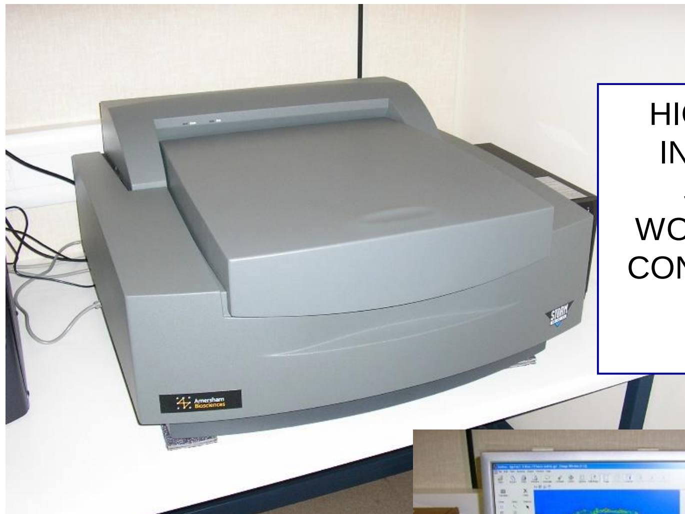
Analytical Techniques (To Date)

- Optical and SEM petrography;
- X-ray radiography
- Digital storage phosphor imaging plate autoradiography (total radioactivity)
- Etch track radiography (alpha autoradiography)
- ICP-OES and ICP-MS
- Powder XRD
- Glancing incidence XRD
- Synchrotron microfocus XRF and XANES

Digital Autoradiography

Eu-DOPED BaFBr IN POLYURETHANE STORAGE PHOSPHOR IMAGING PLATE [various sizes + formats]





HIGH RESOLUTION INFRARED LASER SCANNER AND WORKSTATION WITH CONTROL AND IMAGE PROCESSING SOFTWARE

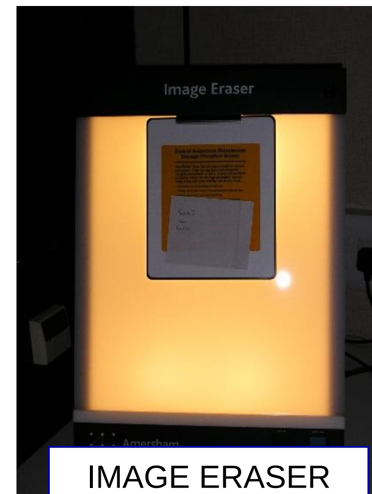
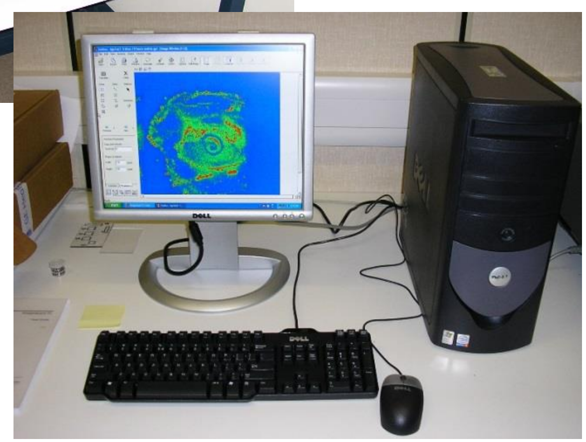
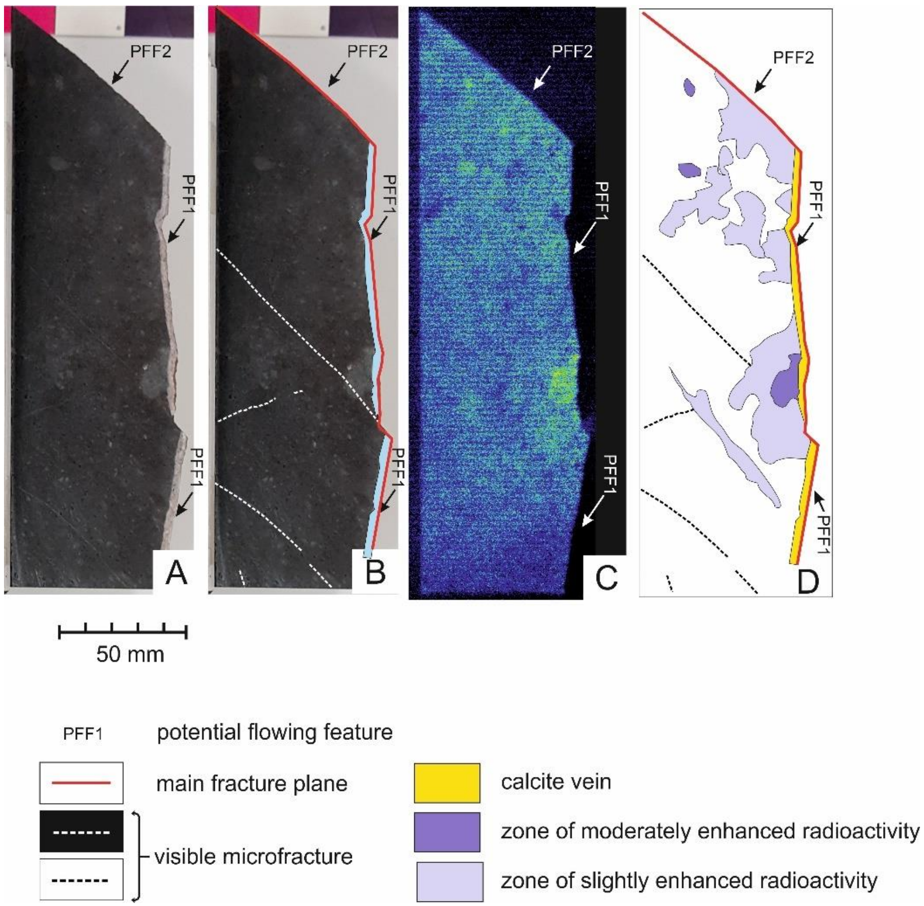


IMAGE ERASER [bright fluorescent light source]

LIGHT-TIGHT EXPOSURE CASSETTE [or ‘Dark Box’]

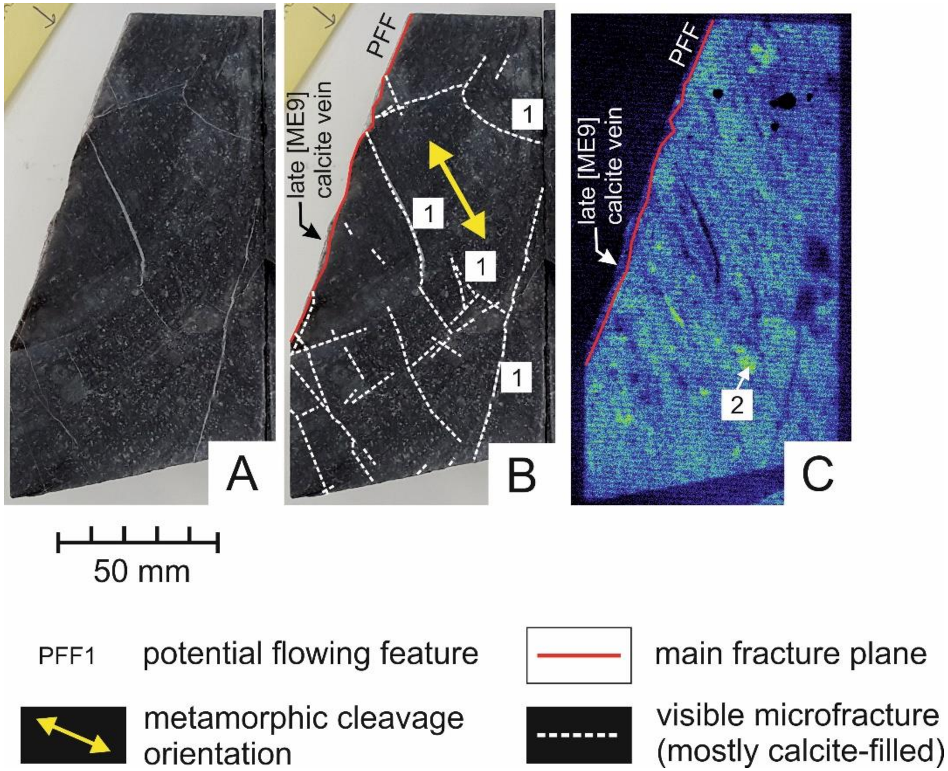


BVG: SSK70953, RCM3 999.6 m



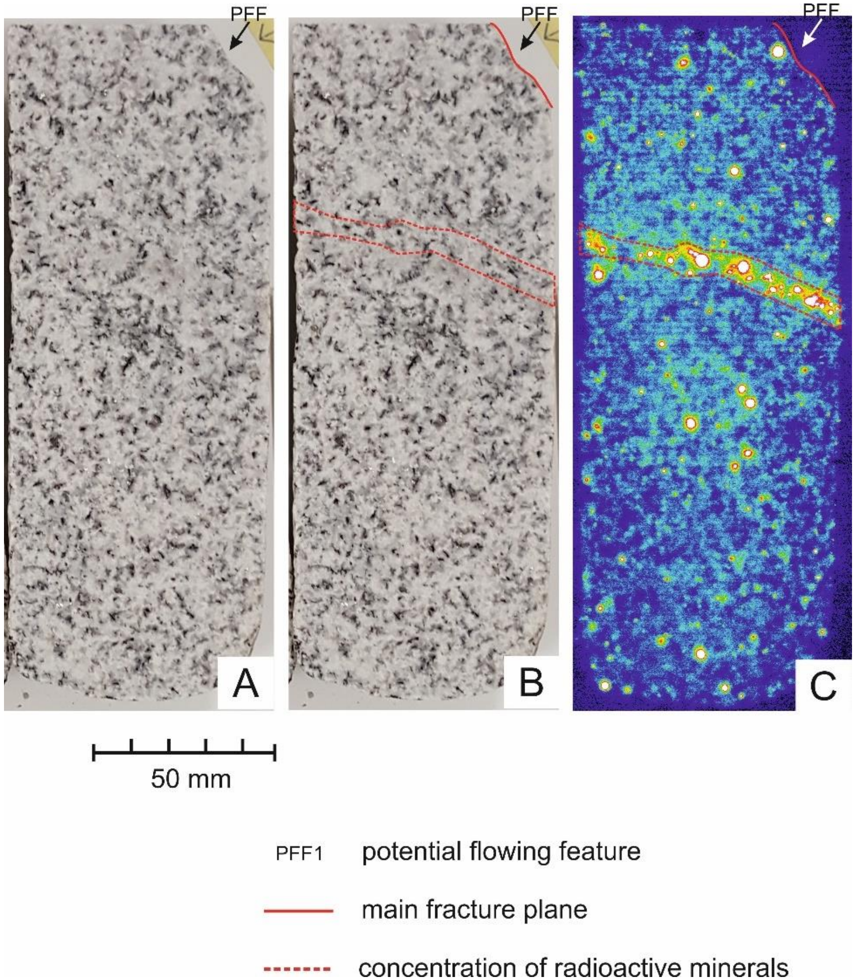
- Weakly radioactive: mostly related to γ-activity from K-minerals (K-feldspar, white mica)
- Rare "hot-spots" correspond to detrital heavy minerals – e.g. zircon.
- Slight hematitisation adjacent to the PFF corresponds to v. slight total enhancement of diffuse radioactivity associated with hematite / hematitised chlorite – patchy, controlled by cleavage fabric

BVG: SSK70953, BH9A 463.42 m



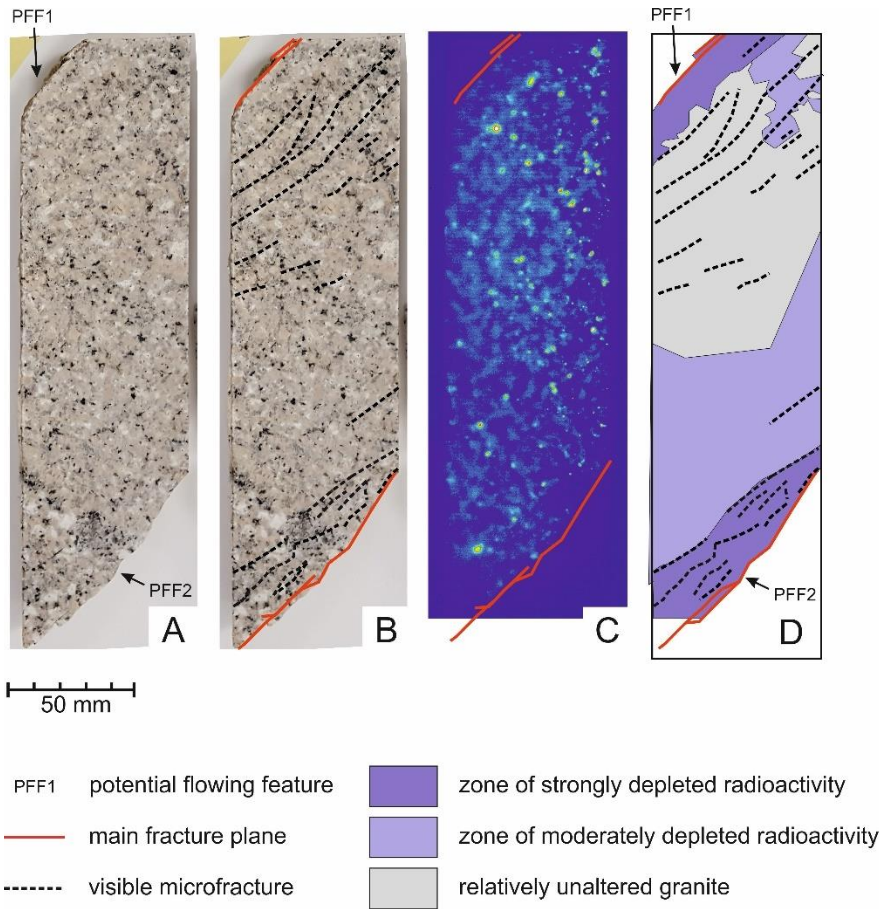
- Weakly radioactive: mostly related to γ-activity from K-minerals (K-feldspar, white mica)
- Rare "hot-spots" correspond to detrital heavy minerals, e.g. zircon
- Strong microfracture network, often calcite-mineralised
- Strong cleavage / metamorphic fabric defines γ-activity distribution (mica)
- No radioactivity in vein calcite
- No evidence of PFF affecting radioactivity distribution

Carnmenellis Granite, 2373.8 m



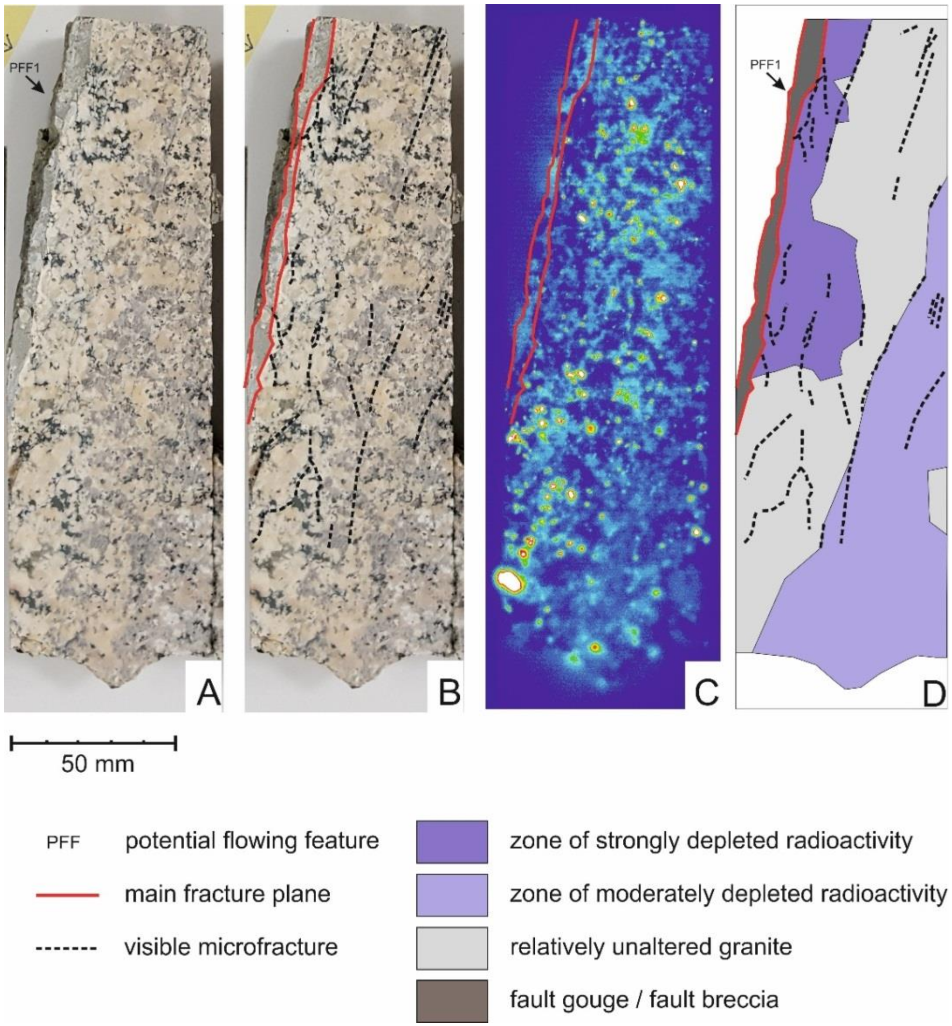
- Radioactive
- Little alteration (pervasive alteration)
- Abundant discrete radioactive ‘hot-spots, associated with primary accessory U-Th minerals: uraninite-thorianite solid-solution (*uranothorianite/thorian uraninite*), zircon, monazite, apatite
- Low-level diffuse γ-radioactivity from potassium minerals (^{40}K)
- Artifact at sample edges from sample geometry (γ-radioactivity)
- No evidence of PFF on wallrock alteration or distribution of radioactivity

Toki Granite, MIU3-8, 555.88 m



- Moderately radioactive
- Alteration zone penetrating wallrock from 2 PFFs
- Microfractures adjacent to PFFs
- Abundant discrete highly-radioactive “hot-spots”
- Low-level diffuse γ-radioactivity from potassium minerals (^{40}K)
- Artifact at sample edges from sample geometry (γ-radioactivity)
- Radioactivity depleted for 10-20 mm adjacent to PFFs

Toki Granite, MIU3-10, 522.47 m



- Strongly radioactive
- Alteration zone pervasive through whole sample
- Intense microfracture network adjacent to PFF – controls alteration
- Abundant discrete highly-radioactive “hot-spots”
- Low-level diffuse γ-radioactivity from potassium minerals (^{40}K)
- Artifact at sample edges from sample geometry (γ-radioactivity)
- Radioactivity depleted for 10-20 mm adjacent to PFF, but diffuse activity enhanced within alteration zone further into the matrix

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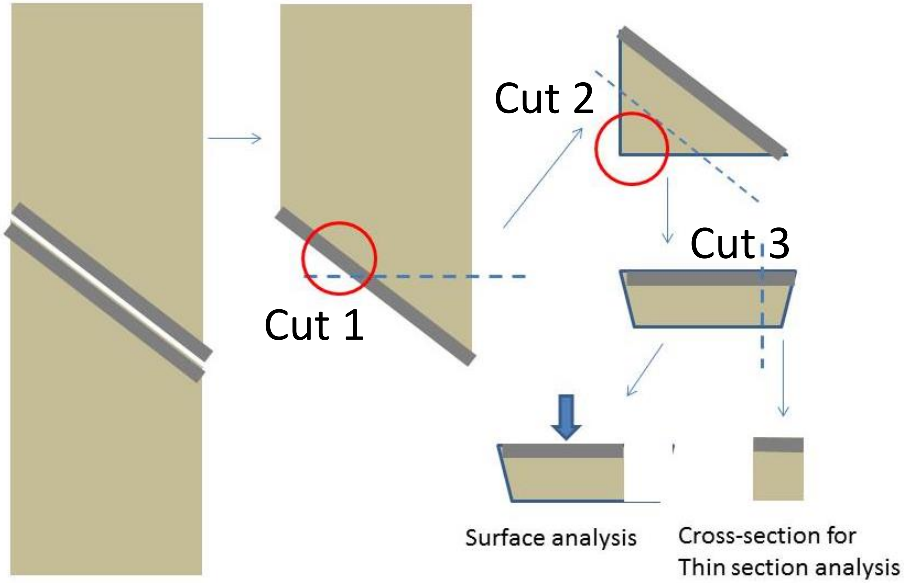
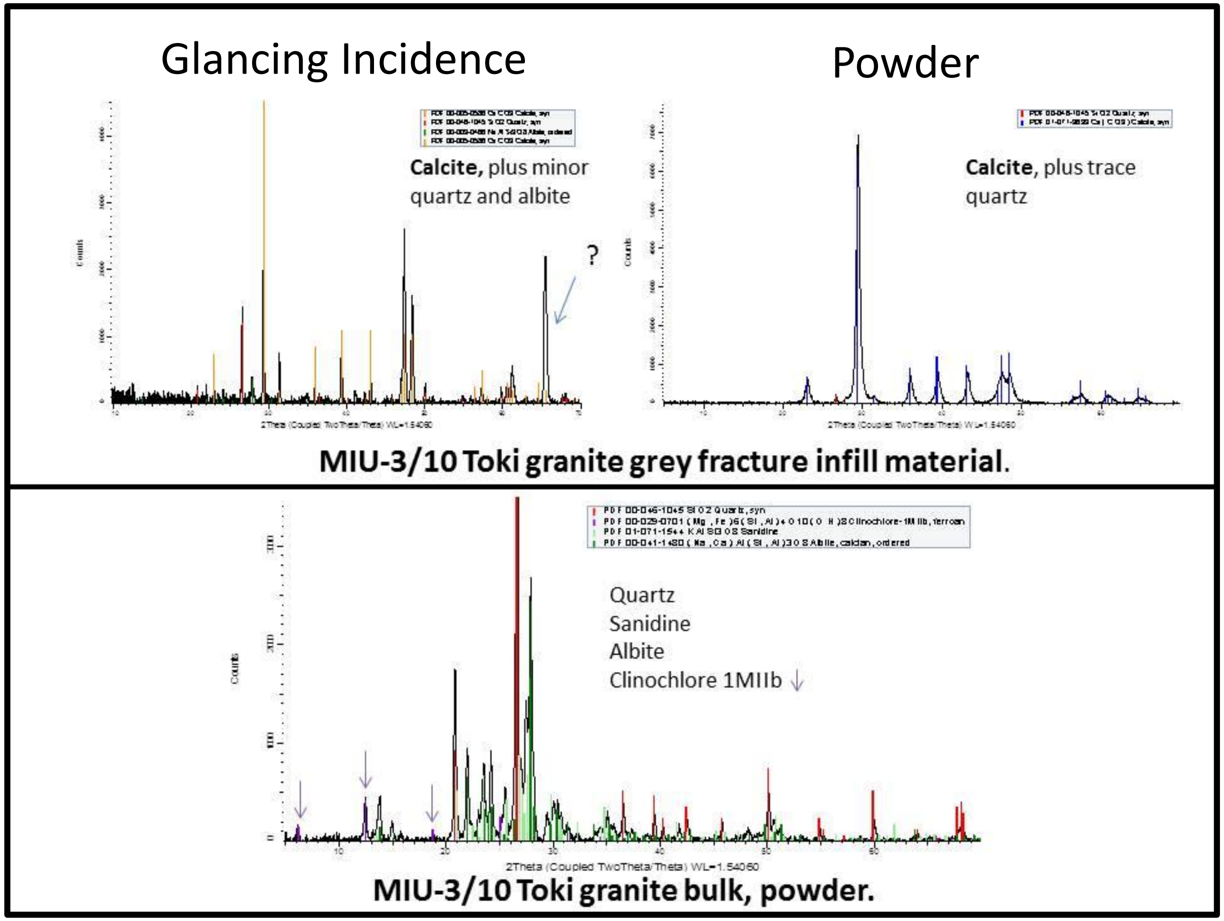
Sample Preparation



- Light brown - unreacted bulk rock
- Grey - altered fracture/infill region
- Blue arrow – fracture surface
- Cut 1 gives wedge with large fracture surface
  - 75% of fracture surface in remaining pieces
  - Fragments from friable fracture infill retained, ball-milled giving powder for XRD
- Cut 2 gives flat-bottom to fracture infill, small chips to be ball-milled giving powder for XRD
- Cut 3 produced two parts
  - one can be mounted, thin sectioned perpendicular to fracture
  - One can be mounted for glancing incidence XRD, ESEM, or other surface analytical method

Glancing Incidence, Powder XRD



MIU-3/10 Toki granite grey fracture infill material.

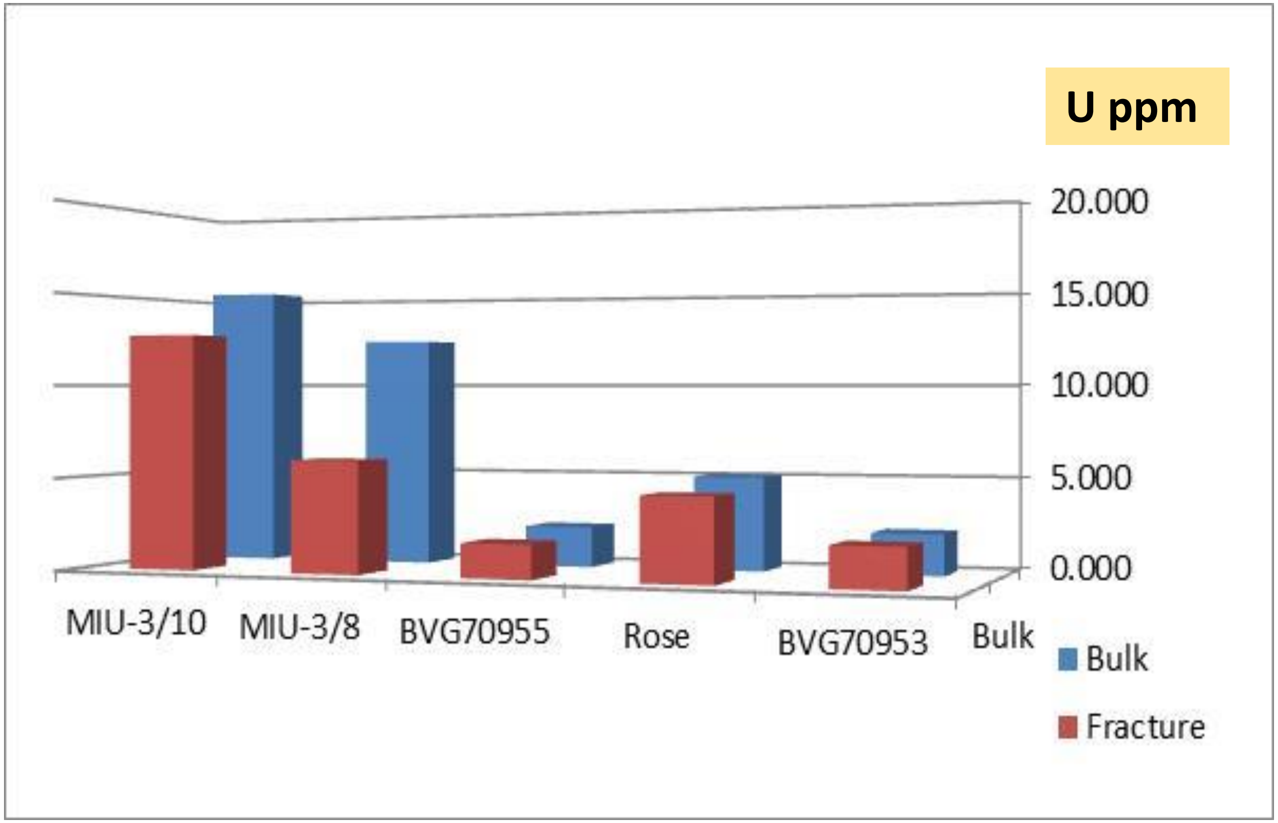
MIU-3/10 Toki granite bulk, powder.

- Powder – bulk mineral analysis
- Glancing incidence involves varying incidence angle of X-ray beam
- Comparison provides insights into nature of minerals coating fracture surfaces

Summary XRD Results

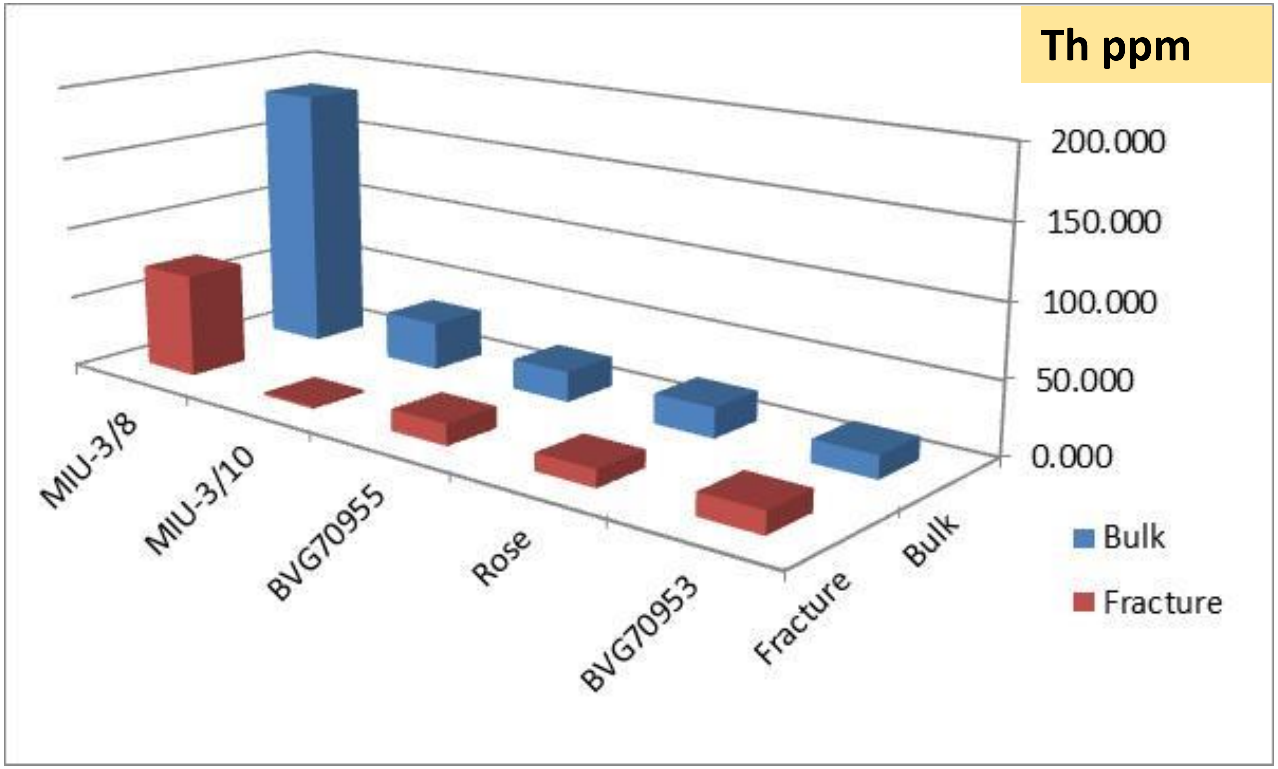
			Qtz	Plag.	K-spar	Biotite	Clinochlore	Calcite	Sericite (Musc)	Hematite	TiO_2*
Borrowdale Tuff	Well developed	Bulk	x	x	x		x	x	x	x	
	70953	Infill	x	x	x		x	xx	xx	x	
	Patchy	Bulk	x	x	x		x				
	70955	Infill	x	x	x		xxx	xxx	x		
Toki Granite	Well developed	Bulk	x	x	x		x				
	"3/10"	Infill	xx	x	x		x	xxx	x		
	Less developed	Bulk	x	x	x	x	x				
	"3/8"	Infill	xx	x	x		x				
Rosemanowes		Bulk	x	x	x		x	x	x		
	70951	Infill	x	x	x			?			x

ICP-MS Analysis - 1



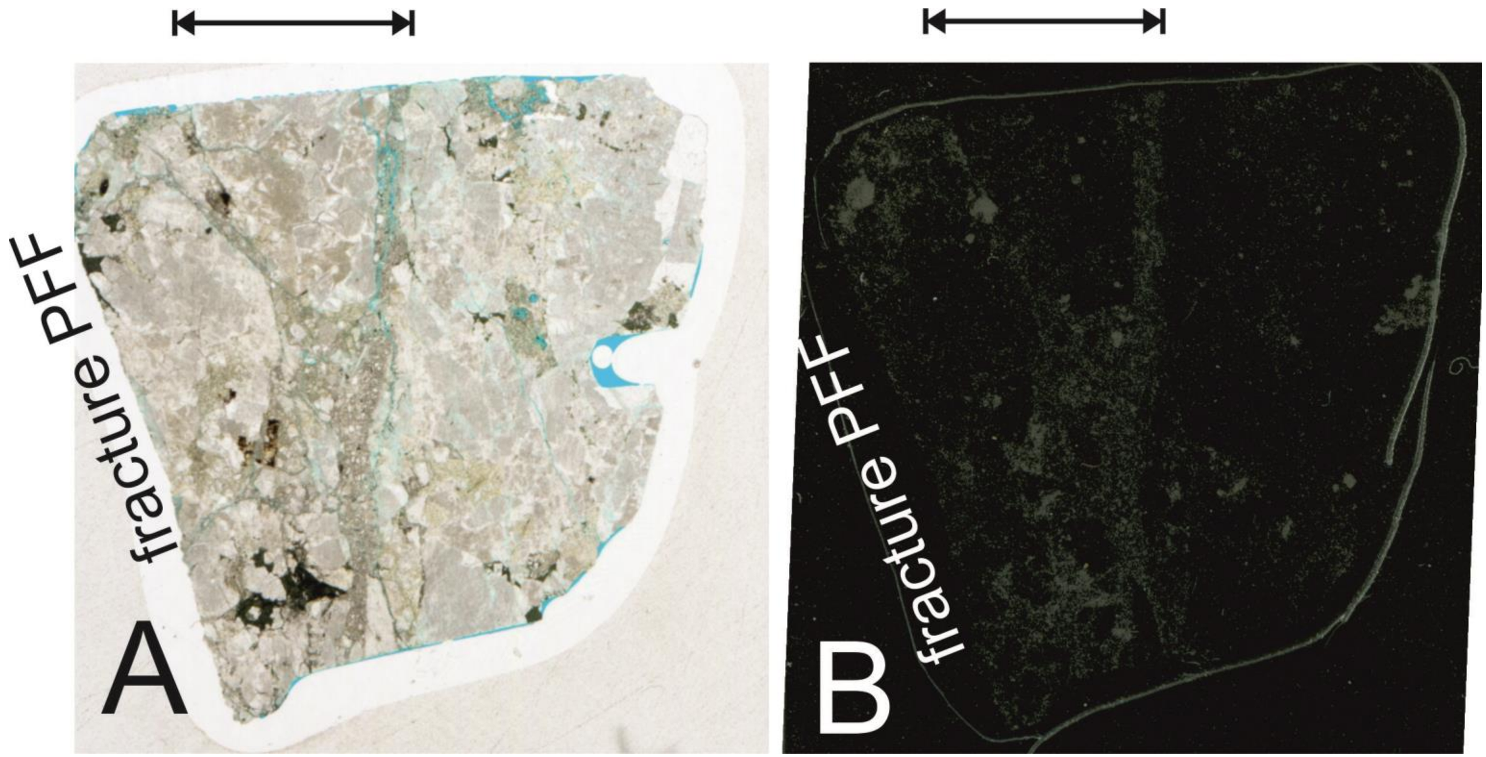
- BVG and Carnmenellis Granite:
  - Little U depletion adjacent to fractures
- Toki Granite:
  - Depletion of U adjacent to fractures
  - Implies hydrolysis / breakdown of primary phases & mobilized U

ICP-MS Analysis -2



- BVG and Carnmenellis Granite:
  - Little Th depletion adjacent to fractures
- Toki Granite:
  - Depletion of Th adjacent to fractures
  - Implies hydrolysis / breakdown of primary phases & mobilized Th

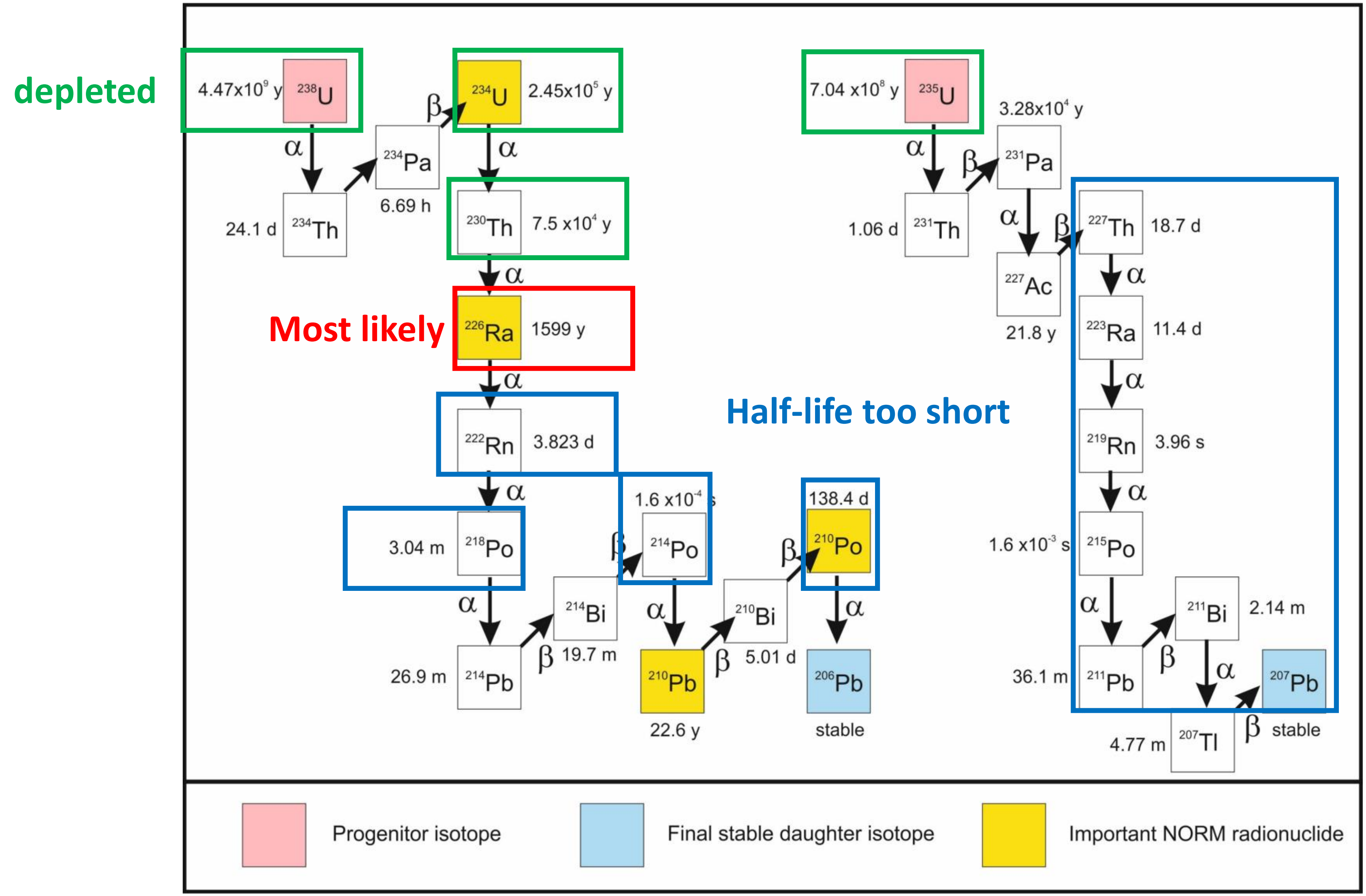
Alpha autoradiography



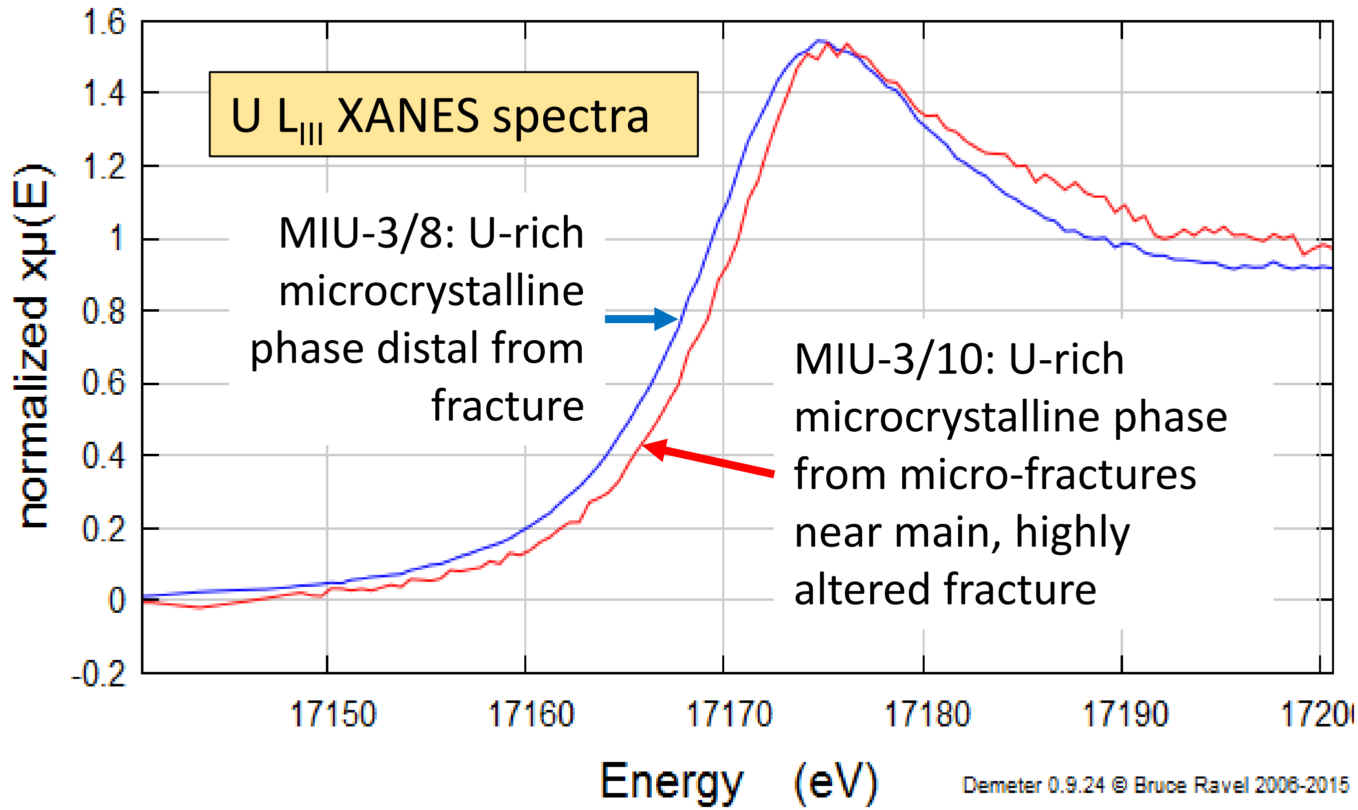
Toki Granite [MIU3/10]

- ICP-MS shows overall loss of U and Th in altered wallrock compared to bulk rock. However, total α-radioactivity is markedly enhanced
- Enhanced radioactivity due to uptake of Ra [from groundwater flowing in the fracture]?

Candidate alpha emitters



Synchrotron Analysis (I18, DLS)



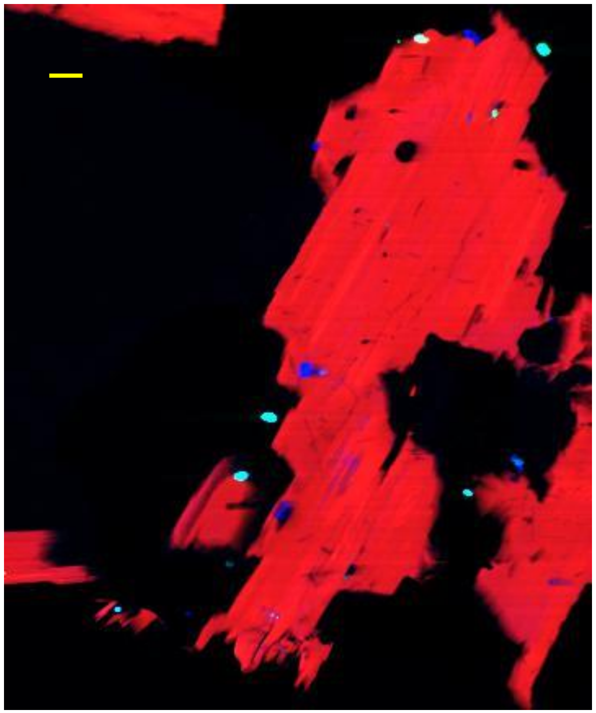
- Energy displacement of curves = ~ 1.5 eV
- Indicates U in MIU-3/10 grain more oxidized (U^{+4} - U^{+6} edge difference is ~1.5 eV)

Synchrotron microfocus XRF images, 5 μm resolution

(Scan 85529)

100 μm scale bars

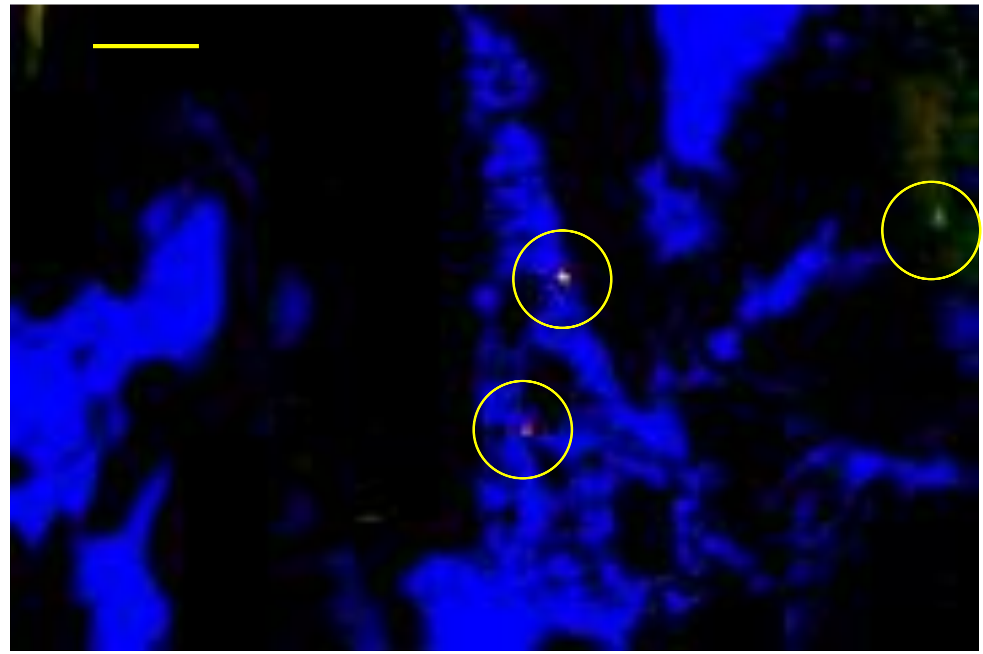
MIU-3/8



Fe Th U

Biotite with
Th/U accessory phases

MIU-3/10



Th U Ca

Fracture infill calcite with
small Th/U secondary grains

Preliminary Conclusions

- The studied mobilization / retardation of radionuclides occurred under natural conditions:
  - The study complements in-situ and laboratory experiments
- Work has demonstrated:
  - close association between uptake/loss of radionuclides and altered wall rock
  - heterogeneous radionuclide uptake / loss, even in similar rocks close together
- Several questions are highlighted which we are continuing to investigate:

Outstanding Questions

- How do natural radionuclides and their analogues occur in the studied rocks?
  - Adsorbed on surfaces?
  - Incorporated into specific mineral grains?
- Were grain boundaries pathways for migration of water / solutes between larger flowing fractures and rock matrix? If so:
  - What was grain boundary / microfracture - major water-conducting feature connectivity?
  - Over what spatial scales?
  - Can we distinguish advective and diffusive transport?
- Have primary variations in spatial distributions of natural radionuclides / analogues influenced their mobility during alteration?
- What relationship exists between spatial variations in concentrations of natural radionuclides / analogues and secondary alteration?
- What does the spatial distribution of secondary alteration indicate about mass transport from / to fractures?

Next Steps

- Further interpretation of existing (large) synchrotron dataset
- Detailed investigation of micro-structures (μ-CT)
  - spatial distribution / frequencies
  - geometry
  - interconnectivity
- Map in detail spatial distributions of radionuclides / analogues /chemical tracers for fluid migration (EPMA)
- Map radioactivity around structures investigated by μ-CT (Autoradiography)
- Map mineralogical indicators of past fluid migration (e.g. Fe-oxyhydroxides, carbonate minerals, clays) around structures investigated by μ-CT (SEM)
- Development of conceptual models for radionuclide uptake by HSR:
  - Interpret results of this analogue study in context of published lab / in-situ studies