Evaluating Interactions of Fracturing Fluids and Degradation Products with Radionuclides Contained in Organic-rich Solid-phase Host Materials

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science for a changing world

NORM in Produced Waters:

Analogue studies, characterization of bedrock, radionuclide occurrence, geochemistry, & wastes

- Characterize U, Ra, other isotope ratios and mixtures in the produced waters. What isotopes account for the radioactivity?
- Determine U and Ra-226 occurrence in the solid matrix of the black shale to gain understanding of the source and the potential for mobilization
- Define or design benchtop experiments and/or models to predict likely changes in produced water concentrations of radionuclides (U, Th ,or Ra) on the basis of leaching experiments
- Is increase in rate of entry of radionuclide wastes into liquid matrixes indicated? Can it be modeled? Does it provide deeper understanding of solid material degradation processes?
- Weathering processes from black shales from near surface exposures as analogues for deeper “gas” shales?

NORM in produced waters:

Analogue Studies, Characterization of Bedrock Radionuclide occurrence, Geochemical factors, and wastes

- Isotopic forensics for wastes – to study processes, precise measurements needed of variations in concentrations and isotope ratios
- Characterize and monitor changes in the already produced wastes: brines, pipe scale, sludges, salts.
- Design leaching/degradation experiments based on information percieved from waste monitoring and analogue studies

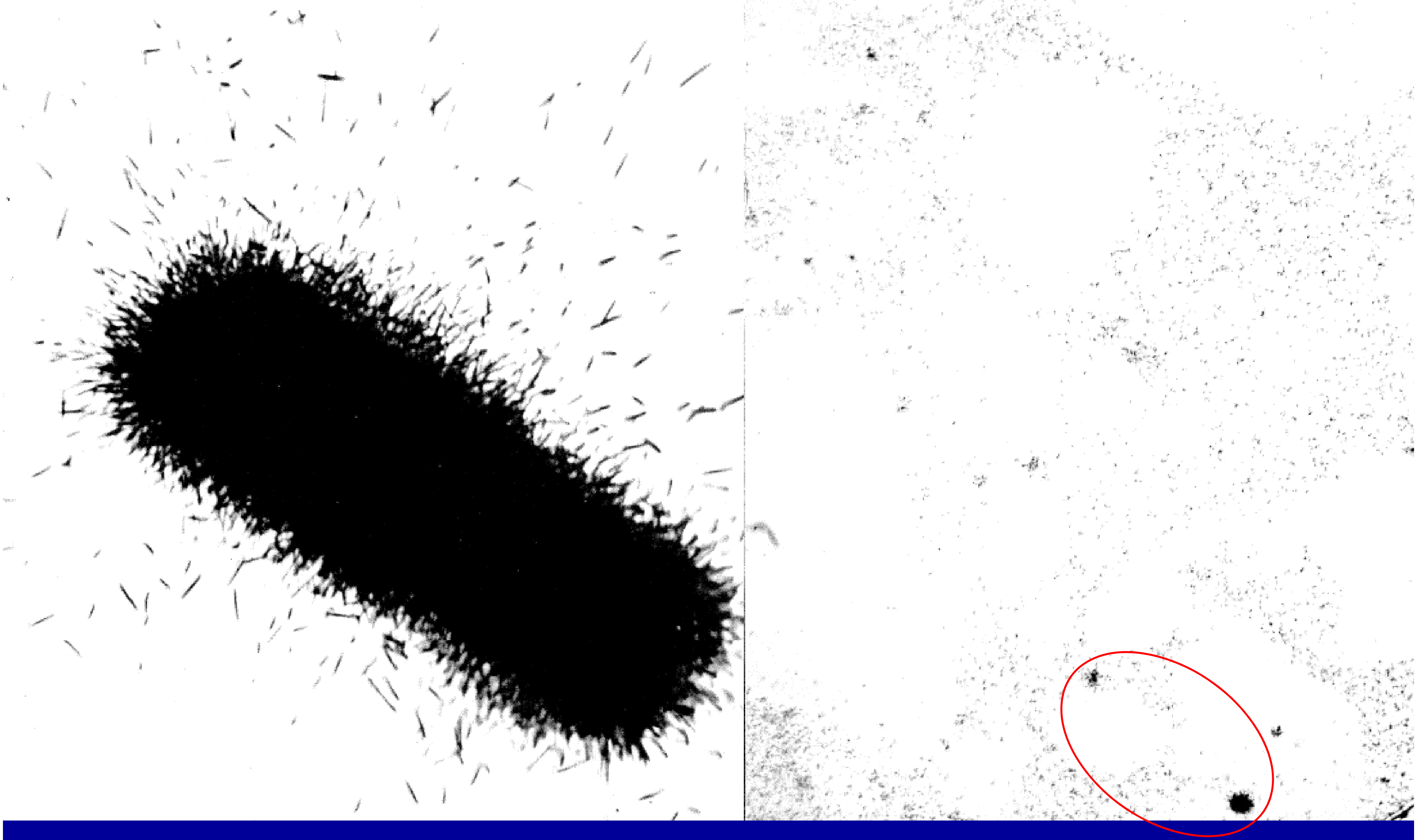
Tools for Analysis for Monitoring Radionuclides in the Solid Matrix

- Auto-Radiography
- Fission-Track Radiography
- Scanning electron microscopy energy dispersive x-ray (SEM/EDX)
- X-ray absorption near edge spectroscopy - monitoring change in speciation/atom coordination
- -microfocused X-ray Fluorescence (uSXRF) microfocused X-ray absorption near edge spectroscopy (uXANES) from focused synchrotron beam (Brookhaven National Lab; Stanford Synchrotron Radiation Lightsource)
- -Organic Molecular analysis of U-organo matrix

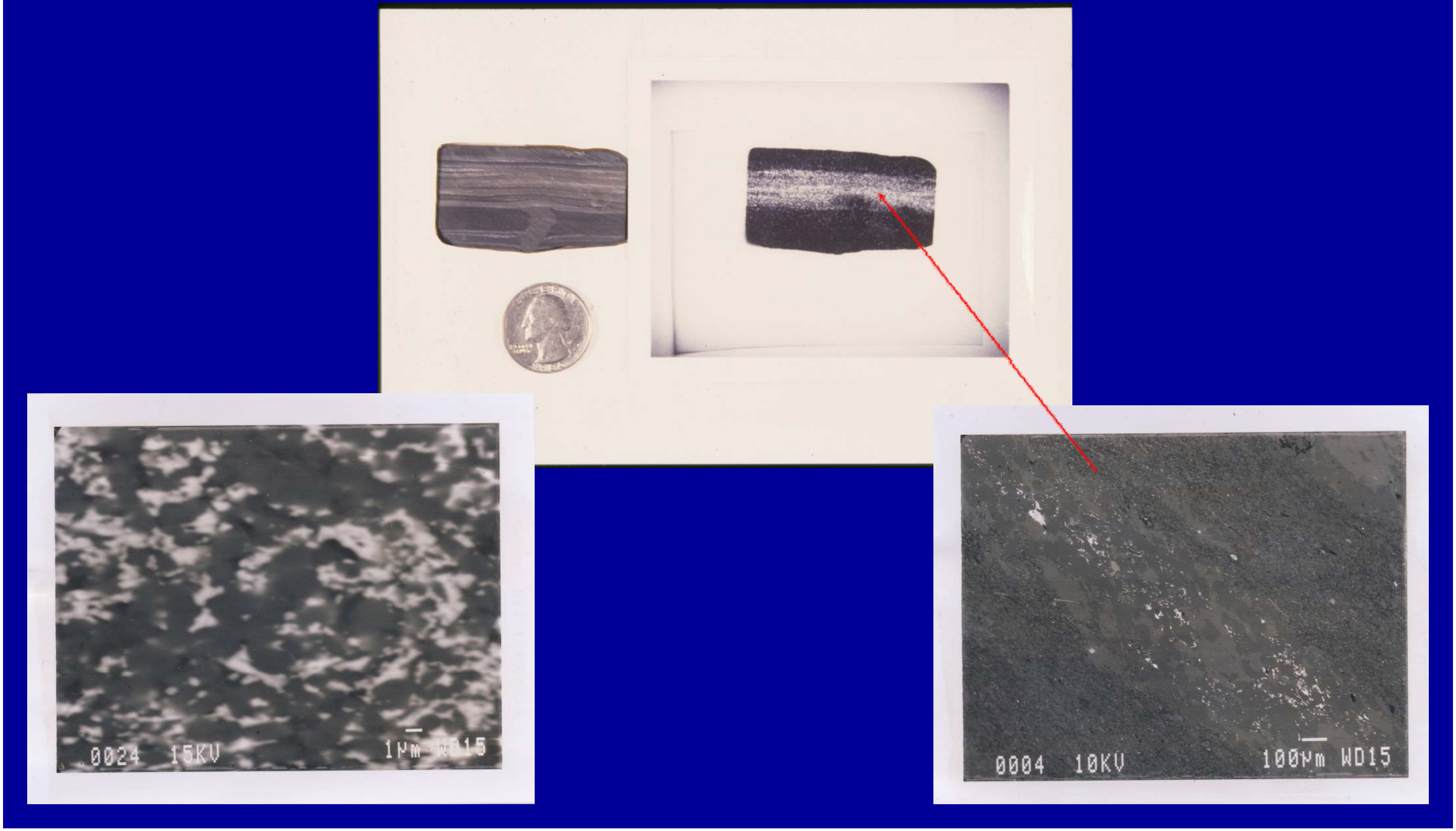
Leaching/degradation experiments

- Distribution in solids before and after leaching
- Ongoing Isotopic monitoring of evolving liquids with precise measurements
- Possible ongoing solids characterization during leaching experiments? (using synchrotron lightsource)
- Characterize organo-U complexes

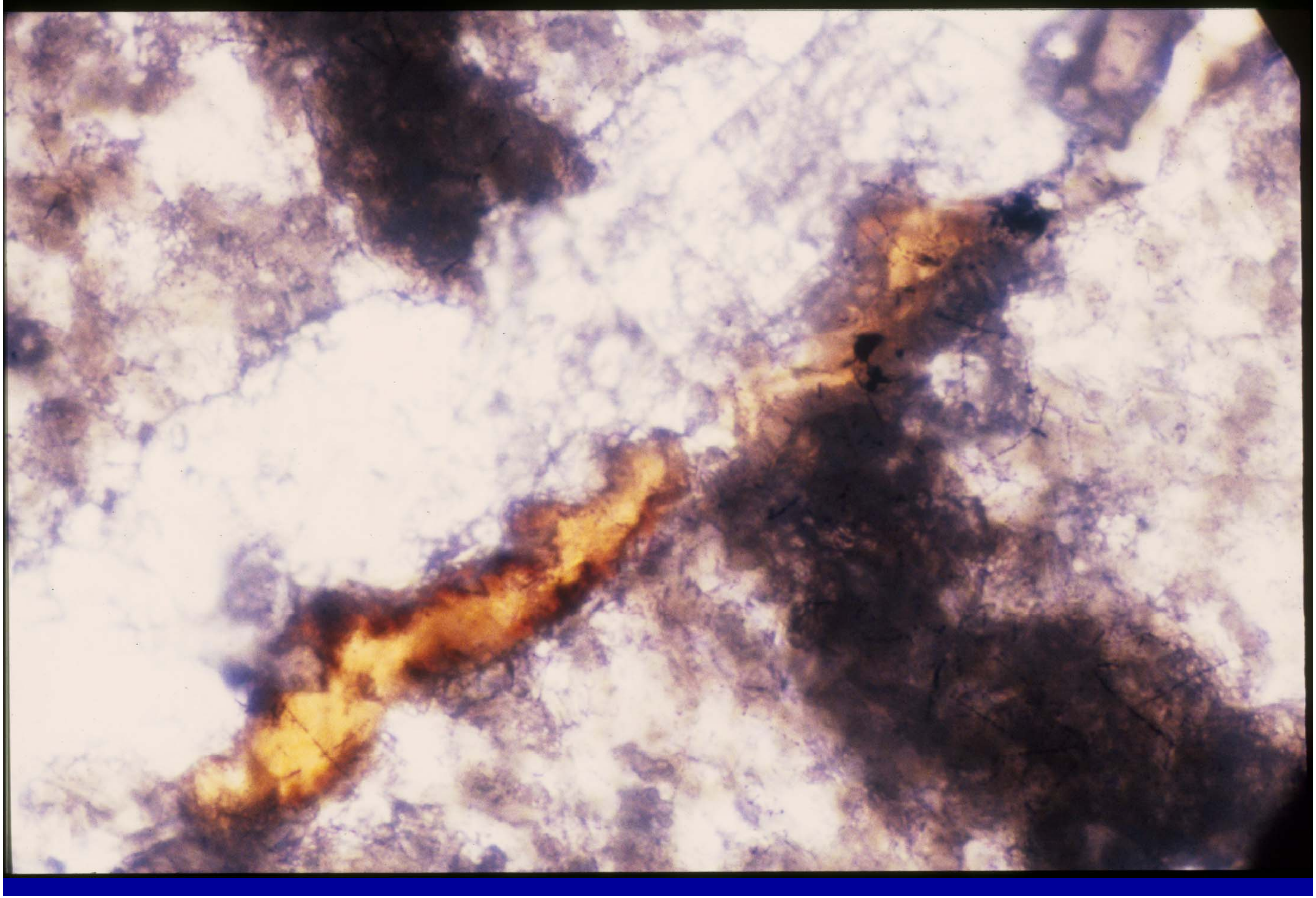
Fission Track Autoradioagraphy (U fission stimulated & imaged)
Despite high U in zircon grain, most U is in grain coatings



Shallow black shale. In places, U distributed evenly in matrix; surprising local reconcentration found in carbonate-replaced zones. Implications for mineralogy & transport? (SEM/EDX + autoradiograph images



Autoradiograph: Radionuclides redistributed in oxides in fractures



Additional findings from analouge studies

-Radionuclides concentrated along pressure solution fronts

These zones may be enhanced zones of fluids migration

-Radionuclides associate with secondary minerals, including pyrite. If true, drilling spoils disposal is an issue (acid drainage and radionuclide mobilization issues)

Design of any process study (leaching?) experiments needs pre-existing information of distribution in solids; unlikely that the process behavior will be the same with respect to various modes of occurrence in the solids

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In situ contaminants (arsenic, radionuclides, or others) can be released from organic-rich gas-bearing shale host rock when fracturing fluids are injected. This potential release raises questions regarding the nature of wastes created and pumped to surface, and those remaining in the formation. The rate of entry of various radionuclides into return flow liquid matrixes can be studied in the laboratory and matched with corresponding observations in the field to estimate the reactions and their rates, and provide understanding of the solid material degradation processes.

Radionuclides can serve as tracers for rock-matrix degradation processes in both field- and laboratory-based experiments. Uranium (U) and thorium (Th) have multiple isotopes and multiple direct and indirect progeny that also have many isotopes. Concentrations of many of these isotopes, their ratios, or ratios of progeny can be determined and monitored in water or brine to estimate changes in U and Th concentrations in rock. Laboratory characterizations can be utilized to determine sources of U in the solids matrix and to show changes in the distribution of U or progeny radionuclides before and after manipulation (for example, simulated fracking of core materials tested by a variety of laboratory approaches). The combination of simultaneous or near simultaneous solid phase and liquid phase observation of the fate of these materials in the presence of laboratory manipulations with the capacity to make similar observations in the field make for a powerful tool for the study of the rock-matrix degradation processes. The characterization of U occurrence in black shales and its fate has already received attention and will provide useful analogues for design of such experiments.

A variety of tools are available for determination of radionuclide occurrences in samples of host rock. Solid phase analysis of the relative abundance of a suite of radionuclides (^{238}U, ^{226}Ra, ^{228}Ra and ^{210}Pb) may include low energy gamma-ray spectrometry that can provide simultaneous, non-destructive determinations in representative samples and important baseline concentration information. The drawbacks to using low energy gamma-ray spectrometry are a large sample size is required (150-250 g) and the actual distribution within the sample cannot be determined. Developed fission-track radiographs or alpha-autoradiographs can be observed under a microscope to reveal the sources of U or other alpha-emitting radionuclides in rock samples. Fission-track radiographs are generated by irradiation of a polished thin section with a thermalized neutron flux that causes fission of ^{235}U in the sample. Fission fragments recoiling from the sample surface are detected by covering the sample with a detector material (low U muscovite). Fission-fragments paths are farther developed by etching the dector material with hydrofluoric acid. The developed fission tracks are observed under a microscope. Although Th is a possible source of fission fragments, the sensitivity of Th to thermal neutron fission is much less than that for an equal amount of U. Autoradiographs are images of the sources of emitted alpha particles, but do not have as high sensitivity and resolution as fission track images. An alpha-sensitive photographic emulsion is spread directly over the thin section and the image of the alpha tracks is observed directly under the petrographic microscope. The alpha autoradiograph captures images of radionuclides undergoing active alpha decay as opposed to images induced by the ^{235}U fission noted in fission tracks.

The use of element mapping utilizing a variety of X-ray analysis techniques can be employed for determination of radionuclide (and other trace element) occurrences in small-scale detail in samples of host rock. Scanning electron microscopy energy dispersive x-ray (SEM/EDX) allows for the capture of high resolution high magnification images as well as dispersive X-ray mapping of the occurrence of the element at points within the image where the X-ray beam is focused. Synchrotron-based spatially resolved micro-X-ray fluorescence (µ-SXRF) allows for small-scale element concentration mapping on individual core samples, whereas synchrotron-based X-ray absorption near edge spectroscopy (XANES or µXANES) can be used to deduce elemental valence state and Extended X-ray Absorption Fine Structure (EXAFS or µEXAFS) can allow for analysis of atom coordination (speciation). The most recent efforts have been to obtain images with µ-SXRF mapping on the same spatial point on the rock sample with the X-ray beam while the leaching experiment is in progress, with chemical effluents collected and analyzed from a split sample undergoing the same procedure. These techniques can be done over small areas within a highly polished sample (approximately 0.3 mm^2 area with a step size of 10 µm and a dwell time of 2s per pixel). The dispersed nature of the U in organic-rich fine-grained rocks may pose difficulty for signal resolution. The intense fluorescence peak of iron in samples can cause interferences. Beamline time would need to be obtained at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory or the Stanford Synchrotron Radiation Lightsource at Stanford University. Images of changes in radionuclide distribution and speciation in the core during such experiments could be captured and compared to changes in radionuclide concentrations in leachate from laboratory-based experiments. Radionuclide concentrations in samples collected at varying stages of fracture fluid flowback in the field could be compared to the results of radionuclide distribution determined in the laboratory for leachate and rock. This series of experiments and field-based observations promises to shed light on the mechanisms responsible for the liberation of radionuclides from gas-bearing shale formations by the fluid fracturing process and could guide the understanding the process of rock matrix degradation.