### Synchrotron X-ray Microspectrosopy for Detecting Ra-226 and its Daughters in Tailings and Mill Waste from Uranium Mining Operations

#### Abstract

A study was undertaken by the CNSC to scope the potential utility of spatially resolved, synchrotron-based hard X-ray microbeam techniques for characterizing the distribution, concentration, molecular form and mineral association of key radionuclides prepared from tailings generated from the mining and milling of uranium ores. Thin sections from core samples from the McClean Lake Tailings Management Facility (TMF) in Saskatchewan were prepared and analyzed at the 13-ID-E hard X-ray microprobe at the Advanced Photon Source in Argonne, Illinois, USA. This report provides an assessment of the data collected to evaluate the utility of these techniques for evaluating the distribution of U, Th and Ra in these types of materials. For these three radionuclides, synchrotron X-ray microprobe studies with a focus on evaluating the abundance, distribution and speciation of uranium are clearly feasible and likely to be informative. Detection levels are such that U distributions and associations can easily be established using microfocused X-ray fluorescence and concentrations are high enough for high quality fluorescence mode X-ray absorption fine structure spectroscopy experiments that constrain U molecular species. Coupled microfocused X-ray diffraction also appears to be useful for evaluating associations between U distribution and mineral species. For the other elements, it is highly unlikely that Ra can be detected in these materials at the concentrations present. Thorium was also not conclusively detected, however it is reasonable to speculate that this may not be the case for tailings from other mines where ores may have much higher Th/U ratios than those at McClean Lake.

#### 1. Background

The Canadian Nuclear Safety Commission (CNSC) conducts independent research as part of its regulatory role in the oversight of nuclear facilities, including uranium mines, mills, processing facilities, and waste management facilities. One of the goals of this research is ensure that contaminant levels associated with these facilities are within applicable guidelines and natural background levels to ensure public safety and for minimizing and monitoring any potentially

adverse, long-term environmental impacts. A particular emphasis of these studies is evaluating the stability and form of contaminants associated with tailings and mineralized waste rock generated from the mining and milling of uranium ore. The potential contaminants of concern (COC's) in these tailings can be quite diverse depending on the mineralogy of the ore being mined and include arsenic, molybdenum, nickel and lead containing species. These tailings may also contain significant concentrations of radioactive elements that must be managed over the long term. Characterization of the environmental behavior of these radionuclides is required for long-term management of uranium mine waste and operational releases of various U-238 decay chain radionuclides. Accurate long term modeling of the stability and mobility of these radionuclides requires an understanding of their speciation, mineralogy and mineral associations within mine tailings solids. However, analytical methods that allow researchers to characterize these molecular properties in the solid phase (as opposed to, for example, pore waters) at low concentrations (ppm) and with micrometer spatial resolution are few.

The purpose of this report is to provide the CNSC with an independent evaluation of the potential utility of spatially resolved, synchrotron-based hard X-ray microbeam techniques for characterizing the distribution, concentration, molecular form and mineral association of various radionuclides that may be present in such tailings. Samples for this study were provided by AREVA from the McClean Lake Tailings Management Facility (TMF) in situ monitoring program and thin sections were prepared. CNSC researchers selected these samples as being representative of the samples that the CNSC is generally interested in for characterizing tailings and waste material throughout Canada. These thin sections were analyzed by CNSC scientific staff at beamline 13-ID-E at the Advanced Photon Source (APS), Argonne National Laboratory, U.S.A. through an APS general user proposal submitted by the CNSC. This report provides an independent evaluation of the data collected with the very specific goal of providing guidance on the future utility of these analytical methods for characterizing the distributions, associations and forms of radionuclides in these types of samples generally. As such, although a very general evaluation of the data collected is provided in this report, the goal is not to draw conclusions regarding the geochemistry of contaminants at the McClean Lake TMF. Rather the focus is on providing recommendations based upon these result for future studies that could be undertaken on these types of materials using these methods, specifically for characterizing radionuclides, and most specifically uranium, thorium and radium.

# 2. Overview of synchrotron-based hard X-ray microbeam techniques in characterizing contaminants of concern in mine tailings

Synchrotron based methods, particular X-ray absorption fine-structure spectroscopy (XAFS), have proven extremely useful in studies of tailings and mineralized waste rock generated from mining of Canadian uranium ore tailings. These XAFS studies have provided unique insights regarding the molecular speciation of COC's in these tailings. At McClean Lake and nearby mining sites a number of studies have employed XAFS techniques to characterize the molecular forms of COC's such as arsenic (Warner and Rowson, 2007; Chen et al., 2009; Essilfie-Dughan et al., 2013; Moldovan et al., 2003), nickel (Essilfie-Dughan et al., 2011, 2012) and molybdenum (Hayes et al., 2014; Blanchard et al., 2015) that persist in these tailings. Microbeam synchrotronbased hard X-ray techniques offer researchers the opportunity to interrogate such materials at the micrometer scale, rather than at the bulk scale, using microbeam X-ray fluorescence (µXRF), absorption fine-structure spectroscopy (µXAFS) and diffraction (µXRD) analysis. Bulk XAFS is invaluable for characterizing the average speciation for COC's at environmentally relevant spatial scales. Microbeam synchrotron methods provide complimentary information for these elements, potentially providing researchers insights regarding specific reactions associated with specific mineralogy at the micrometer scale. Such spatially resolved data can help define the specific reactions that govern how COC's are adsorbed or bound to specific mineralogies or types of organic matter (Walker et al., 2011). These types of insights can be difficult to evaluate using bulk techniques alone at environmentally relevant concentrations.

#### 3. Methods

A good overview of microscopic X-ray fluorescence analysis with synchrotron radiation sources is provided by Adams et al. (Adams et al., 2011) and Sutton et al. (Sutton et al., 2002a). Hard Xray microprobe beamlines are available at a number of synchrotron user facilities internationally and available instruments make use of different available X-ray sources. This includes instruments that use either bending magnet and insertion device X-ray sources at these facilities (Sham and Rivers, 2002; Sutton et al., 2002b). Although instrumental configurations at these beamlines tend to be generally similar, differences exist in X-ray optical layout and detectors that can impact detection sensitivities for trace element analysis and achievable spatial resolutions. The references cited above provide more in depth discussions of relevant differences and capabilities.

For this study CNSC researchers conducted experiments using the GSECARS 13-ID-E X-ray microprobe at the Advanced Photon Source, Argonne National Laboratory, USA. This beamline utilizes Kirkpatrick-Baez focusing mirrors and a 3<sup>rd</sup> generation undulator X-ray source. While the recommendations provided in this report are most directly relevant to this beamline for the analysis specifically of these types of materials (tailings from uranium mining operations), the recommendations should be generally applicable to other similarly configured microprobes worldwide.

The 13-ID-E beamline utilizes a 3.6 cm period undulator X-ray source that provides X radiation from 2.3 to 28 keV. Monochromatic radiation is provided by a cryogenically-cooled doublecrystal monochromator that sits upstream of two horizontally deflecting mirrors with variable mirror coatings that focus the monochromatic beam to a secondary source aperture. The monochromator has fixed offset and utilizes a state-of-the-art, air-bearing turntable for highly stable rotations throughout the range of selectable energies. The system incorporates both Si(111) and Si(311) crystals which are translated into the beam as needed. The Si(111) crystal set was used for these analyses. For this experiment incident flux was measured to be ~  $3.5e^{10}$ photons/second at an incident beam energy of 19 keV. This incident beam energy was used for µXRF and µXRD compositional analysis and mapping of the thin sections prepared from McClean Lake tailings. However, in scoping detection limits for the radionuclides of interest (U, Th and Ra) select areas of these thin sections were also mapped at multiple energies bracketing both the  $L_2$  and  $L_3$  absorption edges. The motivation being that while spectral overlaps from other elements may be present on the emission lines being monitored for elemental detection, conducting analyses above and below both the L<sub>2</sub> and L<sub>3</sub> absorption edges potentially allows limits of detection to be better evaluated.

Beam focusing to the sample is provided by a set of 240 mm long, highly polished, silicon mirrors in a Kirkpatrick-Baez (KB) geometry (Eng et al., 1998). These focusing mirrors allow for grazing incidence focusing using either bare Si or Rh stripes. For these experiments Rh was used to provide the best focusing with the highest intensity. Focused spot size on the sample for these experiments was  $\sim 2 \,\mu m \ge 2 \,\mu m$ . Fluorescence intensities collected for compositional

mapping and spectroscopy were normalized to incident X-ray beam intensity ( $I_0$ ) measured in a helium-filled, 200 mm long ion chamber just upstream of the KB mirror optics.

All data were collected in fluorescence mode using a four-element, silicon-drift-diode detector array (Vortex-ME4, Hitachi High-Technologies Science America, Inc.) with pulse-processing provided by an Xspress 3 digital X-ray processor system (Quantum Detectors). This detector system and pulse processing electronics provide the ability to measure XRF at extremely high count rates (theoretically approaching 3 million counts per second), while also maintaining good energy resolution on the measured energy dispersive spectra. At the Mn K-alpha emission line this system provides an energy resolution of ~150 eV at moderate count rates. Arguably detector systems such as that described here are the most commonly employed at hard X-ray microprobes worldwide. While the energy resolution provided by such energy-dispersive detection can generate complicated spectra with multiple spectral interferences in real world samples, the high count rates and ability to maintain good resolution are generally more highly desired. Other detector systems, for example systems using wavelength dispersive detection, theoretically can provide better "energy" resolution for separating emission lines that strongly overlap (Rivers and Sutton, 1995). However such systems generally sacrifice detection speed and sensitivity so that it is uncommon to routinely see such systems in use.

While absolute detection limits below 1 fg can theoretically be achieved for atomic numbers above 26 using synchrotron based  $\mu$ XRF instruments (Adams et al., 2011), in practicality detection limits are highly dependent on the individual experimental conditions and most importantly on measured spectral backgrounds and overlaps for the elements of interest in the specific materials being analyzed (in this case epoxy-impregnated thin sections of McClean Lake mine tailings mounted on quartz glass slides and encapsulated in 8 $\mu$ m thick kapton film). To help evaluate detection limits under the analysis conditions used in this study (19 keV incident beam energy with stated absorber configuration) several standards were also analyzed as part of the study. This includes NIST XRF thin film standards SRM1832 and 1833 and NBS uranium glasses K-0373, K-0375, and K-0546. These standards were used to calculate minimum detection limits for U, Th and Ra (which have L $\alpha_1$  emission lines at 13.6, 13.0, and 12.3 keV respectively). The minimum detection limit (MDL) for a given element in a sample for XRF analysis can be defined as the minimum concentration at which the X-line intensity equals three times the standard deviation of the background in spectrum under the given experimental conditions. For Pb measured on the L $\alpha_1$  emission line (based on analysis of SRM1833) an MDL of approximately 5 ppm for an accumulation time of 300 seconds can be calculated. For U (based on analysis of NBS glass standard K-0373, 0.05 wt. % U in a Na and Ba enriched silicate glass) a similar MDL between 1-5 ppm for collection times of 300 seconds can be calculated. It's reasonable to assume that Ra and Th would have similar detection limits under these conditions if present in similar matrices. This evaluation, however, ignores the impact of spectral overlaps that arise from the complex chemistry found in these mine tailings samples. It is in fact these spectral overlaps, many of which are difficult or impossible to filter out from the analyses, which most significantly limit detection sensitivity for Ra, Th and U in these samples.

Of the radionuclides of interest in this study only uranium was detected at concentrations high enough for high quality  $\mu$ XAFS analysis. For these  $\mu$ XAFS analyses, analysis was conducted at the U L<sub>3</sub> edge, ~17166 eV. Uranium L<sub>3</sub>-edge  $\mu$ XAFS spectra discussed below were collected by scanning the incident beam from 17086-17156 eV in 5 eV steps, 17156-17179 eV in 0.25 eV steps and from 17179-17326 eV in 2 eV steps at 4 seconds per energy point. For uranium spectroscopy the monochromator calibration was checked using an yttrium metal foil (measured in transmission), which provided an absorption edge energy ( $E_0$ ) of 17038.0 eV (first derivative of the edge). All data were corrected for detector dead time. Uranium standards in the U<sup>6+</sup> oxidation state measured under similar configuration provide an  $E_0$  of 17170.4 eV (Guo et al., 2016).

For measuring X-ray diffraction a Perkin Elmer XRD1621 digital flat panel detector was used, placed in transmission geometry ~ 400 mm downstream of the sample. The XRD1621 detector uses a of 41 x 41 cm amorphous silicon sensor with a 2048 x 2048 sensor size. The XRD1621 provides 200  $\mu$ m pixel resolutions at 1 x 1 binning, frame rates of 15 fps at 1 x 1 binning and 30 fps at 2 x 2 binning. In the coupled  $\mu$ XRF/ $\mu$ XRD mapping mode, both the XRF and XRD detectors are triggered by trigger pulses generated from a Newport XPS motor controller that is used to control sample stage motion. An XPS controller trigger pulse generated for each pixel is routed to the channel advance input of a Struck SIS3820 multichannel scaler which in turn is routed to the trigger inputs of the Xspress 3 and XRD1621 systems. For the studies presented here the area detector positioning covers a *Q* range up to ~ 5 Å<sup>-1</sup>. All  $\mu$ XRD area detector frames

were processed and calibrated using the Dioptas program (Prescher and Prakapenka, 2015). The area detector was calibrated against a CeO<sub>2</sub> powder standard using an incident beam energy of 19 keV, a pixel size of 400  $\mu$ m (2x2 binning), and a sample to detector distance of 492.7 mm.

#### 4. Sample Description

Samples consisted of thin sections of cores collected from boreholes sampled as part of the geochemical program at the McClean Lake Tailings Management Facility (TMF) in 2008.

The licensee for McClean Lake, AREVA Resources Canada Inc., carries out a tailings preparation process whereby ferric sulfate and barium chloride are added to the tailings at specific pHs to precipitate metals. The tailings are placed into the pit at a near-neutral pH. The treatment process has mainly focused on the removal of arsenic. AREVA carries out synchrotron-based research on the tailings to identify As controlling phases; there has been no documented work on synchrotron-based analysis for U in Saskatchewan mine tailings facilities.

Sections were prepared by Vancouver Petrographics Ltd. (Langley, BC, Canada) as epoxy impregnated sections 30-60  $\mu$ m thick and mounted to quartz glass slides. Eight samples were prepared for synchrotron analysis: four samples are from TMF elevations of approximately 369 masl, and four are from approximately 400 masl. (masl, metres above sea level). Concentrations of U in tailings solids in the samples analyzed were reported to vary from 41 – 649 ppm ( $\mu$ g/g). Concentrations of Ra and Th were not available. In associated porewater samples from the TMF in 2008, median concentrations of the three radionuclides were 3.2 Bq/L Ra-226, 1.0 Bq/L Th-230 and 143.5 Bq/L U (5,692  $\mu$ g/L uranium as measured, equal to 70.3 Bq/L U-238, 70.0 Bq/L U-234, 3.2 Bq/L U-235, calculated from natural specific activity). TMF 08-01 is the central borehole; the other samples came from a ring of boreholes around the centre of the TMF. In 2008, the tailings solids surface was at a depth of ~ 420 masl.

Sample Code	Depth (masl)	Uranium (ppm)
TMF 08-01-SA19	369	649
TMF 08-01-SA05	400	41
TMF 08-02-SA16	369	306
TMF 08-02-SA05	400	125
TMF 08-03-SA16	369	504

TMF 08-03-SA05	400	248
TMF 08-04-SA14	369	511
TMF 08-04-SA04	400	309

Of these TMF 08-01-SA19, TMF 08-02-SA05, TMF 08-03-SA05, TMF 08-03-SA16, and TMF 08-01-SA19 were evaluated. Due to APS policy regarding analysis of radioactive materials (which these samples were defined as), all thin sections were encapsulated in a single layer of 8 µm thick kapton film for analysis. In estimating fluorescence detection for quantification a modified version of the program NRLXRF (Criss et al., 1978) was used to account for absorption, including sample to detector air path, and to calculate fluorescence yields given sample matrix and general composition, corrected accordingly for excitation probability and self-absorption effects (He and Van Espen, 1991).

#### 5. Detection of U, Th and Ra XRF emissions in McClean Lake TMF thin sections

As mentioned, based on standard analysis it can be expected that in simple matrices (assuming densities of ~2.5 g/cc and thin section thickness) with low to moderate spectral backgrounds, U, Th and Ra should be detectable using L fluorescence lines at concentrations of a few ppm. If these radionuclides are present in the solid phase within these tailings at these concentrations (which may not be true for all three elements), the primary consideration for scoping the detectable limits for analysis of U, Th and Ra is largely the degree to which spectral backgrounds and overlaps from other elements present in the samples can be deconvoluted within the resolution of the energy dispersive detector system being used.

It is therefore useful to establish what elements are most commonly observed in these tailings samples at thin section scale to constrain the most likely overlaps that are likely to interfere with detection of U, Th and Ra. To facilitate this process energy dispersive spectra were summed (Figure 1) from roughly 0.2 mm<sup>2</sup> areas extracted from 1.5 mm<sup>2</sup> compositional maps of samples TMF01-SA19-Map2, TMF02-SA05-Map4, TMF03-SA05-Map5, and TMF03-SA16-Map3. (Figures 2-5). These compositional maps were all collected using an incident beam energy of 19 keV, raster scanning the samples continuously and bi-directionally through the focused X-ray

beam with XRF energy dispersive spectra being collected from the detector system every 2  $\mu$ m with a dwell dime of 40 msec per pixel.

For this exercise these ~  $0.2 \text{ mm}^2$  area summed energy dispersive spectra were selected visually from the larger compositional maps in an effort to encompass as broad a range in mineralogy as possible, which is admittedly somewhat subjective. It is apparent from these spectra (Figure 1) that X-ray fluorescence from Fe (K lines), Ni (K lines), As (K lines) and Pb (L lines) are notably intense between 3 and 19 keV under the operating conditions in all four samples. Other K-line emissions common to all four samples include those from K, Ca, Ti, Cr, Mn, Cu, Zn, Rb and Sr. L-line emissions seen in all samples include those from Ba (although an overlap with Ti K emission lines needs to be deconvoluted) and U. In two samples, sample TMF02-SA05-Map4 in particular, Bi L fluorescence is also detected in the summed spectra.

Of the three particular radionuclides of interest, U is clearly detectable in all samples at the concentrations present, even though there is a notable overlap of the U L $\alpha_1$  emission line with that of Rb K $\alpha$ . The energy separation of 218 eV between these two emission lines makes them relatively straightforward to resolve accurately at the detector energy resolution, particularly since it appears that on average the overall U concentrations in these maps appear to exceed those of Rb. Based on emission intensities measured in U enriched glasses (adjusting fluorescence yields to account for the differences in matrix composition, sample thickness and absorption characteristics between the glasses and the tailings sample using the program NRLXRF from Criss et al., 1978) it can be estimated that these randomly selected 0.2 mm<sup>2</sup> areas contain between ~ 150 and 400 ppm U, in reasonable agreement with the reported values from analysis of bulk tailings solids.

Attempts to detect Th and Ra L emission lines in these tailings samples proved unsuccessful due to their much lower concentrations (compared to U) coupled with difficulties in resolving these emission lines from those of Pb, Bi, Zr and, at high Fe concentrations, the Fe K detector pileup (sum) peaks. The energies of these emission lines are shown for reference in Figure 1 in red for comparison to peaks from detected elements. To best evaluate if Ra L emission lines are detectable, a series of XRF compositional maps were also generated by setting the incident beam energy so that the Ra L<sub>3</sub> and Ra L<sub>2</sub> absorption edges were bracketed. This allowed more sensitive evaluation of any potential differences in XRF fluorescence intensities for the Ra L $\alpha_1$  and L $\beta_1$  emission lines as their relative absorption edges are traversed in small energy increments, monitoring for changes in fluorescence counts for the portions of the energy dispersive spectra binned to include these emission lines. In all cases no L fluorescence emissions (alpha or beta) from Ra were detected. It can generally be concluded that given the likely Ra concentration present in the solid phase of these tailings samples and considering the strong spectral overlaps in particular from Pb (which is ubiquitously present at relatively high concentration in all samples) that detection of Ra L fluorescence is highly unlikely in these materials using synchrotron micro XRF energy dispersive analysis if Ra concentrations are at the few ppm level or lower.

Thorium fluorescence was also not detected in these particular samples, for similar reasons. Th  $L\alpha_1$  strongly overlaps with L $\beta$  peaks of Pb and Bi, both of which are seen in these materials, and includes overlaps with Fe K $\alpha$  pileup peaks. The Th  $L\beta_1$  peak suffers from fewer spectral overlaps, but the potential for detecting Th at the  $L_2$  edge was not fully met in these experiments since incident beam energies were kept below the Th  $L_2$  edge (19.693 keV). This could be more fully explored in future studies but based on the data available to date, Th was not detectable at the concentrations present in these particular samples.

Thus of the three radionuclides of particular interest, U, Th and Ra, it is generally concluded that synchrotron X-ray microprobe studies that focus on evaluating the distribution and speciation of uranium are clearly feasible and likely to prove productive and informative. It is generally concluded that it is highly unlikely that Ra can be detected in these materials at the concentrations present using these techniques. Similarly Th is not conclusively detected in these samples, however it is reasonable to speculate that this may not be the case for tailings from other Canadian mines where ores may much higher Th/U ratios than those seen at McClean Lake.

## 6. Recommendations for future synchrotron X-ray microprobe analysis of uranium species in samples similar to those from McClean Lake TMF

Having established that synchrotron X-ray microprobe studies that focus on evaluating the distribution and speciation of uranium in thin section samples similar to those collected from the McClean Lake TMF are likely to prove the most productive and informative for studying

radionuclides, it is useful to evaluate what geochemical and mineralogical data can potentially be obtained in future studies based on the preliminary results obtained in this study. Assuming the use of beamlines with capabilities and instrumentation similar to those of 13-ID-E, several specific analytical research directions could be focused on simultaneously. This includes:

- µXRF analysis of thin section samples to evaluate uranium distribution and concentration at micrometer scale and to evaluate any potential elemental associations that may exist with U in these samples.
- 2. µXRD analysis for constraining sample mineralogy. Questions that could potentially be addressed would be are crystallographically distinct uranium minerals identifiable and do these likely represent pre-existing ore mineral or phases formed during ore processing or after residence in the TMF? For U that is not present as an essential structural component in a U mineral phase, is U distribution correlated to the distribution of other mineral phases in these tailings?
- µXAFS analysis of U to evaluate both the oxidation state of uranium and to constrain potential molecular species for uranium.

All three analytical directions can be useful for evaluating long term environmental risks and for predicting geochemical controls on uranium speciation and mobility in the future. Such data can potentially be useful for identifying U binding and/or sorption sites and for predicting geochemical changes over time. The data collected as part of this study provide preliminary examples of how each of these approaches can be employed in answering such questions. Preliminary evaluation of these three analytical approaches is provided below with recommendations for future studies.

## 6.1 µXRF analysis of thin section samples to evaluate uranium distribution and elemental associations at micrometer scale

As described, energy dispersive XRF data were collected for several thin sections in mapping mode. Figures 2-5 show fluorescence intensities for selected X-ray emission lines (K, Ca, Ti, Fe, and Ni K $\alpha$ , As K $\beta$ , Pb L $\beta_1$  and U L $\alpha_1$ ) shown as two dimensional, grayscale maps. These intensities represent total counts accumulated within 40 msec accumulation time binned over a range of detector channels defined as representatively including the emission line of interest, summed over the four detector elements of the ME-4 SDD detector, corrected for detector dead time and normalized to incident flux (I<sub>0</sub>). In each map the displayed counts are scaled so that the lowest 5% intensities are uniformly set to black and highest 5% of intensities are uniformly set to white. This avoids issues with visualizing only very high concentration points (i.e. hot spots) in the map and obtaining a more realistic picture of elemental distribution overall. However, since in this case the grayscale scaling is defined relative to the maximum and minimum count rate for each X-ray emission, maps cannot be compared so as to visualize relative differences in elemental concentration between elements or samples. This could be done in future studies if needed.

It's also worth mentioning that by only showing a set of binned channels, potential spectral overlaps may not be well accounted for. For most of the maps displayed here, given the elements selected for display, this generally isn't a significant issue. But this can be better evaluated in the future through peak fitting of the energy dispersive spectra, which may provide better visualization for given peaks where overlaps do exist.

In the maps shown many elements, particularly K, Fe, As, Pb, Ni and U, appear broadly distributed within particulate masses 100's of micrometers in size. These particulate masses are particularly well defined in samples TMF01-SA19-Map2 and TMF03-SA16-Map3 (Figures 2 and 5). Smaller particulates 10's of micrometers in diameter containing all these elements at higher elemental concentration are also observed along with small particulates enriched in Ca and Ti. High U abundance particles 10's of micrometers in size are observed in all four samples at concentrations that are a factor of 10 or more higher than that observed in the larger diffuse masses.

Uranium is clearly detectable in all these samples at concentrations easily detected by synchrotron  $\mu$ XRF. For future studies such  $\mu$ XRF analyses should allow the evaluation of differences in U distribution among different particle types and, coupled to  $\mu$ XRD and  $\mu$ XAFS, would allow researchers to evaluate if differing forms of uranium are associated with each particle type, with distinct mineral phases and if any of these high U particulates represent distinct U bearing minerals. Based on these maps, no clear preliminary elemental associations can be identified between U and other elements in these samples, although further detailed analysis may better define any associations that may exist. That being said, some spatially localized associations can be observed in this preliminary data set. For example in map TMF03-SA05-Map5 an area of elevated Ti concentration (Figure 4a) is clearly associated with high abundances of U (Figure 4b). The  $\mu$ XRD data collected on this area (Figure 9) shows that this high Ti area is dominated by anatase (TiO<sub>2</sub>) and that U is observed both within and surrounding this mineral. This is the only area where this association was clearly identified and thus may not be particularly representative of the larger geochemical correlations that may exist across samples more generally. Further studies would be useful for defining trends that may exist.

#### 6.2 µXRD analysis for constraining sample mineralogy in relation to U distribution

Given that U is observable in all the samples examined as part of this study, coupled µXRFµXRD analysis can potentially be used to evaluate if crystallographically distinct uranium bearing minerals are identifiable and to provide information as to whether U distribution is correlated with the occurrence of specific non-U mineral phases in these tailings at the micrometer scale. In this study µXRD data were collected in two modes. Firstly single point  $\mu$ XRD spectra (each consisting of a 20 second exposure within a focused 2  $\mu$ m beam spot) were collected for specific points, selected based on distinct chemical signatures of interest observed in the µXRF compositional maps (see Walker et al., 2011 for similar examples). In total 85 such point  $\mu$ XRD spectra were collected. In the second modality  $\mu$ XRD data collected simultaneously along with µXRF data are collected continuously in a mapping mode, with each pixel in the map representing a 100 msec accumulation over a 2 µm pixel in the map, with each map generally being less than 350 µm in the longest dimension (Lanzirotti et al., 2016). Since every map pixel in this modality contains an independent XRD frame, regions of interest can therefore be defined on the map based on unique chemical features and summed to provide an averaged XRD pattern for that area. This takes advantage of the pixel averaging that summation provides to improve statistics and produce more powder like patterns. Four of these maps were collected.

Evaluation of the collected  $\mu$ XRD data that provide interpretable patterns shows that all four samples studied appear dominated by primarily three mineral phases, illite (with small structural variations between samples), hematite, and gypsum. For example, Figure 6 shows an XRF compositional map of TMF02-SA05-Map4 where the fluorescence intensities for Fe K $\alpha$ , As K $\beta$ and U L $\alpha_1$  are all displayed overlain as a red-green-blue (RGB) intensity map. A small high U area (Spot 58) selected for  $\mu$ XRD analysis (defined by the yellow arrow) and integrated is shown in the upper right ( $2\theta$  vs intensity). Comparison to a reference XRD pattern for illite shows that the only identifiable mineral here is this clay phase, which proves to be the most frequently identified mineral by µXRD in the four sections studied. Similarly in map TMF01-SA19-Map2 (Figure 7) a high U abundance area here analyzed by µXRD (Spot 28) can be shown to consist of a mixture of gypsum and illite. In both cases, no uranium bearing minerals can be identified by  $\mu$ XRD even though U concentrations are strongly elevated. Of all the 85  $\mu$ XRD spectra collected no distinct U minerals have been identified to date by diffraction (although further careful evaluation is warranted). It should be emphasized in this respect that the µXRD approach utilized here essentially assumes that mineral phases being interrogated are not amorphous and that they are finely crystalline enough relative to the focused 2µm beam to provide an interpretable, powder diffraction type pattern. Thus the lack of identified U-bearing minerals by µXRD does not necessarily preclude their presence, but does perhaps circumstantially imply that U may be bound or sorbed to other mineral phases or that it dominantly exists as poorly crystalline or amorphous phases. Future studies can better evaluate these observations. In Figure 8, µXRD of high Fe abundance areas (Spot 10) shows that many of such areas often contain hematite as a mineral phase.

Other minor mineral phases, for example anatase or quartz, are also observed and in some cases these minor phases do appear to potentially be areas where U is preferentially localized. Figure 9 shows an RGB XRF map for a small portion of the TMF03-SA05-Map5 maps shown in Figures 4a and 4b. This defines an area that encompasses the highest Ti abundance visible near the center of Figure 4a. This map was collected using coupled continuous  $\mu$ XRF- $\mu$ XRD mapping. As such,  $\mu$ XRD data for specific portions of the map with distinct chemical signatures can be summed to evaluate overall mineralogy for these areas. In Figure 9 integrated diffraction patterns are shown for three such areas. Each area is defined by a dotted dashed yellow outline. The center of this area containing the highest Ti concentrations clearly contains the mineral anatase (upper right). It also contains the highest U concentrations in the area mapped. A high U area to the left appears to consist of a mixture of anatase, hematite and illite (lower left). Again, in both areas no U minerals are identifiable by  $\mu$ XRD. Arsenic enriched areas on the margin of this anatase grain are consistent with the presence of phengite (middle right). Further evaluation of the  $\mu$ XRD data collected as part of this study and similar studies for other samples from this TMF and other sites would be useful for defining any other associations between U distribution and tailing mineralogy that may exist.

#### 6.3 $U L_3 \mu XAFS$ analysis for constraining U oxidation state and speciation

The U abundances present in these samples are high enough, both in areas where U is diffusely distributed and in localized, high U particulates, for high quality U L<sub>3</sub> edge  $\mu$ XAFS data to be collected. Such data can prove invaluable for evaluating what U species may be present in tailings. A number of such spectra were collected as part of this study that help define variations in U oxidation state in these samples, but additional studies focused more specifically on  $\mu$ XAFS would likely prove highly valuable for understanding the geochemical evolution of U in these tailings. Several example spectra are shown here for individual points identified in the collected maps.

For example, Figure 6 shows U X-ray absorption near edge structure (XANES) spectra from four points on map TMF02-SA05-Map4 in the lower right and upper part of the figure. Each analysis point is shown with a dashed yellow circle on the map with an analysis number. These four analyses are collected from three points with high U concentration (53, 59, 60) and one spot (56) where U concentrations are lower. Four additional spectra from a smaller map of TMF02-SA05 are shown in Figure 10, again three from high U particles (1, 2, 3) and one from a lower U area (4). All of these eight spectra are similar and virtually indistinguishable from one another. The  $E_0$ energies of these eight spectra are consistent with the presence of uranium in the  $U^{6+}$  oxidation state and the spectra also show a distinct shoulder centered at 10 to 15 eV above the absorption maximum, often attributed to a multiple-scattering resonance within the linear O=U=O moiety (Hudson et al., 1996). Figure 11 (top) shows an example of this shoulder in a uranyl acetate standard as compared to spectra from a uraninite standard. This feature is less prominent in spot 56. Such differences in the EXAFS portion of the spectra have been noted in other studies and may indicate that, although these points all are consistent with U<sup>6+</sup>, that differing U species may exist or U species with differing equatorial coordination (Reeder et al., 2001). A U XANES analysis from TMF03-SA16-Map3 is shown in Figure 8, showing very similar spectra to those shown in Figures 6 and 10, again consistent with the presence of  $U^{6+}$  species.

In Figure 9 two XANES spectra are shown for U associated with the anatase mineral identified by  $\mu$ XRD and discussed above (TMF03-SA05). One spectra is collected from the highest U

portion of this map and the second from a lower U area that is adjacent. Again, the  $E_0$  energies are both consistent with uranium in the U<sup>6+</sup> oxidation state. However, the EXAFS portions of these two spectra are significantly different from those shown for TMF02-SA05 and TMF03-SA16 (Figure 11 bottom) and again may indicate that although U<sup>6+</sup> appears to be the dominant oxidation state for U in the four samples studied here, that differences likely exist in the U species present.

Some of the XANES spectra collected, although not discussed here, may indicate the presence of more reduced U species, but overall U<sup>6+</sup> seems to dominate. It may be reasonable to speculate that this data may imply that by and large the U found in these tailings likely is not from ore minerals that have escaped U processing, which would be expected to be dominated by U<sup>4+</sup> mineral phases such as uraninite, pitchblende, coffinite, etc. (Fayek et al., 1997). Particularly given that the efficiency of the U-extraction process at these mine sites is stated to generally be greater than 99% (Schindler et al., 2013), we may speculate that the U species observed here ultimately originate from discharged mill-process solutions following chemical extraction which assumed their speciation in the tailings solids. Future XAFS analyses may help address such questions and provide a basis for understanding the long-term stability of the U-phases occurring in tailings.

#### 7. Conclusions

On the basis of the data collected from these thin sections of tailings from the McClean Lake facility it is generally concluded that of the three radionuclides of particular interest to the CNSC, U, Th and Ra, that synchrotron X-ray microprobe studies that focus on evaluating the distribution and speciation of uranium are clearly feasible and likely to prove productive and informative. Uranium abundances are high enough so that elemental distributions and associations can easily be established using  $\mu$ XRF. More importantly, concentrations are high enough for high quality  $\mu$ XAFS experiments to be conducted simultaneously that constrain U molecular species. Such XAFS analyses can potentially be highly useful for understanding the long-term stability of the U-phases occurring in tailings such as these. The preliminary data collected as part of this study shows enough variability in the  $\mu$ XAFS to suggest that multiple species are present. It is also clear that coupled microfocused X-ray diffraction would also be

invaluable to researchers for evaluating associations that may exist between the distribution of U species in these materials and specific mineralogies.

It is also generally concluded that it is highly unlikely that Ra can be detected in these materials at the concentrations present using these techniques. Thorium is also not convincingly detected in these samples, however it is reasonable to speculate that this may not be the case for tailings from other Canadian mines where ores may much higher Th/U ratios than those seen at McClean Lake.

#### **Figure Captions**

<u>Figure 1</u>: Summed energy dispersive spectra extracted from compositional maps of samples TMF01-SA19-Map2 (upper left), TMF02-SA05-Map4 (upper right), TMF03-SA05-Map5 (lower left), and TMF03-SA16-Map3 (lower right). These spectra represent roughly 0.2 mm<sup>2</sup> areas extracted from the larger 1.5 mm<sup>2</sup> compositional maps. Identified X-ray fluorescence emission lines are labeled. Where X-ray emission lines for Ra L $\alpha_1$ , Ra L $\beta_1$ , and Th L $\alpha_1$  would be observed, if present, are labeled in red. The energy at which the Fe Ka pileup peak would occur is also shown.

<u>Figure 2</u>: X-ray fluorescence intensities from a  $1.5 \text{mm}^2$  compositional map of section TMF01-SA19-Map2. (a) Maps for K, Ca, Ti, and Fe K $\alpha$ . (b) Maps for Ni K $\alpha$ , As K $\beta$ , Pb L $\beta_1$  and U L $\alpha_1$ . All maps are displayed as two dimensional grayscale maps, 40 msec accumulation time per 2 $\mu$ m pixel.

<u>Figure 3</u>: X-ray fluorescence intensities from a  $1.5 \text{mm}^2$  compositional map of section TMF02-SA05-Map4. (a) Maps for K, Ca, Ti, and Fe K $\alpha$ . (b) Maps for Ni K $\alpha$ , As K $\beta$ , Pb L $\beta_1$  and U L $\alpha_1$ . All maps are displayed as two dimensional grayscale maps, 40 msec accumulation time per 2 $\mu$ m pixel.

<u>Figure 4</u>: X-ray fluorescence intensities from a  $1.5 \text{mm}^2$  compositional map of section TMF03-SA05-Map5. (a) Maps for K, Ca, Ti, and Fe K $\alpha$ . (b) Maps for Ni K $\alpha$ , As K $\beta$ , Pb L $\beta_1$  and U L $\alpha_1$ . All maps are displayed as two dimensional grayscale maps, 40 msec accumulation time per 2 $\mu$ m pixel.

<u>Figure 5</u>: X-ray fluorescence intensities from a  $1.5 \text{mm}^2$  compositional map of section TMF03-SA16-Map3. (a) Maps for K, Ca, Ti, and Fe K $\alpha$ . (b) Maps for Ni K $\alpha$ , As K $\beta$ , Pb L $\beta_1$  and U L $\alpha_1$ . All maps are displayed as two dimensional grayscale maps, 40 msec accumulation time per 2 $\mu$ m pixel.

<u>Figure 6</u>: Three color XRF intensity map of Fe K $\alpha$  (red), As K $\beta$  (green) and U L $\alpha_1$  (blue) for sample TMF02-SA05. Yellow arrow shows where single point  $\mu$ XRD spectra were collected

with integrated  $2\theta$  vs intensity plot shown in the upper right. Integrated diffraction pattern for this point is shown in blue. Reference pattern for illite is superimposed in red. Yellow numbered circles on the map show where U L<sub>3</sub> µXANES spectra were collected. The measured, edge step normalized µXANES spectra are shown in the lower right. Edge positions are all consistent with U in the 6+ oxidation state.

<u>Figure 7</u>: Three color XRF intensity map of Fe K $\alpha$  (red), As K $\beta$  (green) and U L $\alpha_1$  (blue) for sample TMF01-SA19. Yellow arrow shows where single point  $\mu$ XRD spectra were collected with integrated 2 $\theta$  vs intensity plot shown in the upper right. Integrated diffraction pattern for this point is shown in blue. Reference pattern for illite (red) and gypsum (green) are superimposed.

<u>Figure 8</u>: Three color XRF intensity map of Fe K $\alpha$  (red), As K $\beta$  (green) and U L $\alpha_1$  (blue) for sample TMF03-SA16. Yellow arrow shows where single point  $\mu$ XRD spectra were collected with integrated 2 $\theta$  vs intensity plot shown in the upper right. Integrated diffraction pattern for this point is shown in blue. Reference pattern for hematite is superimposed in red. Yellow numbered circles on the map show where U L<sub>3</sub>  $\mu$ XANES spectra was collected. The measured, edge step normalized  $\mu$ XANES spectra are shown in the lower right. Edge position is consistent with U in the 6+ oxidation state.

<u>Figure 9</u>: Three color XRF intensity map of Fe K $\alpha$  (red), As K $\beta$  (green) and U L $\alpha_1$  (blue) for a localized area of sample TMF03-SA05. This map was collected using coupled continuous  $\mu$ XRF- $\mu$ XRD mapping. The three areas on the map defined with dashed yellow lines show where  $\mu$ XRD data were summed. The integrated diffraction patterns for these three areas are shown in the upper right (with anatase reference pattern), lower left (with anatase, hematite and illite reference patterns), and middle right (with phengite reference pattern). Yellow numbered circles on the map show where U L<sub>3</sub>  $\mu$ XANES spectra were collected. The measured, edge step normalized  $\mu$ XANES spectra are shown in the lower right. Edge positions are consistent with U in the 6+ oxidation state.

<u>Figure 10</u>: Three color XRF intensity map of Fe K $\alpha$  (red), As K $\beta$  (green) and U L $\alpha_1$  (blue) for a localized area of sample TMF02-SA05. Yellow numbered circles on the map show where U L<sub>3</sub>

 $\mu$ XANES spectra were collected. The measured, edge step normalized  $\mu$ XANES spectra are shown to the right. Edge positions are consistent with U in the 6+ oxidation state.

<u>Figure 11</u>: (Top) Comparison of U L<sub>3</sub>  $\mu$ XANES spectra from UO<sub>2</sub> and Uranyl acetate standards. These are example fluorescence mode spectra collected at beamline X26A, National Synchrotron Light Source, Brookhaven National Laboratory. Spectral calibration was adjusted to be coincident with that measured at 13-ID-E. Note that the spectra for U<sup>4+</sup>O<sub>2</sub> is shifted to lower energy than that for (U<sup>6+</sup>O<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O) and that uranlyl acetate displays a distinct shoulder centered at 10 to 15 eV above the absorption maximum. (Bottom) Comparison of U L<sub>3</sub>  $\mu$ XANES spectra from sample TMF01-SA19 with two spectra from TMF03-SA05.

#### Appendix

The data collected in this project have been archived on a USB drive which is physically associated with this document in CNSC records. This Appendix provides a brief guide to the raw data and background information on the samples. Key information files are stored on a USB drive in the subdirectory README of the root directory APS MAPS; these specific files are also directly retrievable from CNSC electronic records. The main data files are not stored in CNSC electronic records and are available by retrieving the USB drive from the physical records.

1. E-DOCS-#4915043-R606.1 Lab Notebook APS Synchrotron Studies 2015

An Adobe PDF file with the hand-written record of the spots on the thin sections that were selected for further analysis. The codes, coordinates and brief comments for these spots are recorded in a scan of the laboratory notebook used for this purpose; the original notebook (#171) is retained at the Advanced Photon Source.

2. E-DOCS-#4963830-R606.1 Pictorial Guide APS Synchrotron Studies 2015

A Microsoft PowerPoint file containing a pictorial guide showing the spots analyzed on the large-scale maps, with simple annotations and pointers. This was prepared from screen captures in sequence as the samples were being investigated; associated comments are in the APS lab notebook as noted above.

- 3. E-DOCS-#3713717-AREVA McClean Lake Tailings Optimization and Validation Program (TOVP), Validation of Long Term Tailings Performance Report (2009) A PDF of AREVA reference documentation for the samples that were analyzed from boreholes in the McClean Lake TMF in 2008. Geochemical data are available for tailings solids and for porewater in associated samples for multiple elements and radionuclides with background information on the nature of the tailings. This reference documentation is updated on a periodic basis; this AREVA submission is from the time when the samples were actually collected.
- 4. E-DOCS-#4852319-R606.1 CNSC Staff notes on 2008 McClean Lake Tailings Thin Sections
  A Microsoft Excel file containing copies of reference materials and further references to

CNSC records with useful information. These are working notes prepared by CNSC staff.

Other subdirectories on the USB stick contain some software packages, data files saved at the time of data collection in 2015, and a few processed data files that have supported interpretation of results to date. These are outlined below for each directory.

#### 1. APS data directory description

The main guide to the data available is the HTML file *sample\_stage.html*, it contains images and coordinates for the samples that were investigated. The directory Sample\_Images contains high resolution JPEG images that this HTML file references. Opening the HTML file and clicking on any image opens the high resolution JPEG.

The main X-ray spectroscopy results for all maps, spots, standards, etc. are named according to the notes in the laboratory notebook and power point guide and are straightforward.

Compositional XRF maps are all found in the **MAPS** directory as binary HDF5 files (\*.H5) readable using the GSECARS program LARCH (<u>http://cars.uchicago.edu/xraylarch/</u>).

All XANES results are found in the root directory, filenames have extensions such as \*.001, \*.002, etc. These are ascii files, the header is self descriptive regarding what is included within data columns for individual energy steps (for example which column represents monochromator energy,  $I_0$ , MCA fluorescence intensities for each detector channel, detector input and output countrates, etc.) These can be viewed and interpreted using a variety of programs designed for analysis of X-ray spectroscopy data, such as the Athena program (Ravel and Newville, 2005).

All XRD data are found in the **XRD** directory as 1024x1024 TIFF image files. These can be processed using a variety of programs available for analysis of X-ray diffraction area detector data, such as Dioptas (Prescher and Prakapenka, 2015). The TIFF files labeled "glass" represent background spectra collected on the thin section with only epoxy on the slide. The CeO<sub>2</sub> files are spectra collected on a cerium dioxide XRD powder standard. The CALIBRATION.PONI file contains the detector calibration calculated using the program DIOPTAS. The included ZIP file and the **INTEGRATED** subdirectory contains integrated 2 $\theta$  vs Intensity data in ascii format (with .XY extensions) for all the area detector data, calculated using DIOPTAS. These files can

be visualized and evaluated using a variety of open source and commercially available XRD processing programs using an incident wavelength 0f 0.652256 angstroms.

Other files such as the \*.MCA files found in the root directory are single point energy dispersive spectra in ascii format (<u>http://cars9.uchicago.edu/software/epics/mcaDoc.html</u>).

#### References

- Adams, F., Vekemans, B., Silversmit, G., De Samber, B., and Vincze, L., 2011, Microscopic Xray Fluorescence Analysis with Synchrotron Radiation Sources, *in* Handbook of Nuclear Chemistry, Springer, p. 1737–1759.
- Blanchard, P.E., Hayes, J.R., Grosvenor, A.P., Rowson, J., Hughes, K., and Brown, C., 2015, Investigating the Geochemical Model for Molybdenum Mineralization in the JEB Tailings Management Facility at McClean Lake, Saskatchewan: An X-ray Absorption Spectroscopy Study: Environmental science & technology, v. 49, p. 6504–6509.
- Chen, N., Jiang, D.T., Cutler, J., Kotzer, T., Jia, Y.F., Demopoulos, G.P., and Rowson, J.W., 2009, Structural characterization of poorly-crystalline scorodite, iron(III)–arsenate coprecipitates and uranium mill neutralized raffinate solids using X-ray absorption fine structure spectroscopy: Geochimica et Cosmochimica Acta, v. 73, p. 3260–3276, doi: 10.1016/j.gca.2009.02.019.
- Criss, J.W., Birks, L.S., and Gilfrich, J.V., 1978, Versatile x-ray analysis program combining fundamental parameters and empirical coefficients: Analytical Chemistry, v. 50, p. 33– 37, doi: 10.1021/ac50023a013.
- Eng, P.J., Newville, M., Rivers, M.L., and Sutton, S.R., 1998, Dynamically figured Kirkpatrick Baez x-ray microfocusing optics, *in* v. 3449, p. 145–156, doi: 10.1117/12.330342.
- Essilfie-Dughan, J., Hendry, M.J., Warner, J., and Kotzer, T., 2013, Arsenic and iron speciation in uranium mine tailings using X-ray absorption spectroscopy: Applied Geochemistry, v. 28, p. 11–18, doi: 10.1016/j.apgeochem.2012.10.022.
- Essilfie-Dughan, J., Hendry, M.J., Warner, J., and Kotzer, T., 2012, Microscale mineralogical characterization of As, Fe, and Ni in uranium mine tailings: Geochimica et Cosmochimica Acta, v. 96, p. 336–352.
- Essilfie-Dughan, J., Hendry, M.J., Warner, J., and Kotzer, T., 2011, Solubility Controls of Arsenic, Nickel, and Iron in Uranium Mine Tailings, *in* Merkel, B. and Schipek, M. eds., The New Uranium Mining Boom, Springer Berlin Heidelberg, Springer Geology, p. 325– 334, http://link.springer.com.proxy.uchicago.edu/chapter/10.1007/978-3-642-22122-4\_38 (accessed February 2016).
- Fayek, M., Janeczek, J., and Ewing, R.C., 1997, Mineral chemistry and oxygen isotopic analyses of uraninite, pitchblende and uranium alteration minerals from the Cigar Lake deposit, Saskatchewan, Canada: Applied Geochemistry, v. 12, p. 549–565, doi: 10.1016/S0883-2927(97)00032-2.
- Guo, X., Tiferet, E., Qi, L., Solomon, J.M., Lanzirotti, A., Newville, M., Engelhard, M.H., Kukkadapu, R.K., Wu, D., and Ilton, E.S., 2016, U (v) in metal uranates: a combined

experimental and theoretical study of MgUO 4, CrUO 4, and FeUO 4: Dalton Transactions,.

- Hayes, J.R., Grosvenor, A.P., Rowson, J., Hughes, K., Frey, R.A., and Reid, J., 2014, Analysis of the Mo Speciation in the JEB Tailings Management Facility at McClean Lake, Saskatchewan: Environmental science & technology, v. 48, p. 4460–4467.
- He, F., and Van Espen, P.J., 1991, General approach for quantitative energy dispersive x-ray fluorescence analysis based on fundamental parameters: Analytical Chemistry, v. 63, p. 2237–2244, doi: 10.1021/ac00020a009.
- Hudson, E.A., Allen, P.G., Terminello, L.J., Denecke, M.A., and Reich, T., 1996, Polarized xray-absorption spectroscopy of the uranyl ion: Comparison of experiment and theory: Physical Review B, v. 54, p. 156.
- Lanzirotti, A., Newville, M., Manoukian, L., and Lange, K., 2016, High-speed, coupled microbeam XRD/XRF/XAFS mapping at GSECARS: APS beamline 13-ID-E: Clays and Clay Minerals, v. 64, in press.
- Moldovan, B.J., Jiang, D.T., and Hendry, M.J., 2003, Mineralogical characterization of arsenic in uranium mine tailings precipitated from iron-rich hydrometallurgical solutions: Environmental science & technology, v. 37, p. 873–879.
- Prescher, C., and Prakapenka, V.B., 2015, DIOPTAS: a program for reduction of twodimensional X-ray diffraction data and data exploration: High Pressure Research, v. 35, p. 223–230, doi: 10.1080/08957959.2015.1059835.
- Ravel, B., and Newville, M., 2005, ATHENA , ARTEMIS , HEPHAESTUS : data analysis for X-ray absorption spectroscopy using IFEFFIT.: Journal of Synchrotron Radiation, v. 12, p. 537–541, doi: 10.1107/S0909049505012719.
- Reeder, R.J., Nugent, M., Tait, C.D., Morris, D.E., Heald, S.M., Beck, K.M., Hess, W.P., and Lanzirotti, A., 2001, Coprecipitation of Uranium(VI) with Calcite: XAFS, micro-XAS, and luminescence characterization: Geochimica et Cosmochimica Acta, v. 65, p. 3491– 3503, doi: 10.1016/S0016-7037(01)00647-0.
- Rivers, M.L., and Sutton, S.R., 1995, A wavelength dispersive detector for synchrotron x -ray fluorescence microprobe analysis: Review of Scientific Instruments, v. 66, p. 1454–1454.
- Schindler, M., Durocher, J.L., Kotzer, T.G., and Hawthorne, F.C., 2013, Uranium-bearing phases in a U-mill disposal site in Northern Canada: Products of the interaction between leachate/raffinate and tailings material: Applied Geochemistry, v. 29, p. 151–161, doi: 10.1016/j.apgeochem.2012.11.007.
- Sham, T.K., and Rivers, M.L., 2002, A Brief Overview of Synchrotron Radiation: Reviews in Mineralogy and Geochemistry, v. 49, p. 117–147, doi: 10.2138/gsrmg.49.1.117.

- Sutton, S.R., Bertsch, P.M., Newville, M., Rivers, M., Lanzirotti, A., and Eng, P., 2002a, Microfluorescence and Microtomography Analyses of Heterogeneous Earth and Environmental Materials: Reviews in Mineralogy and Geochemistry, v. 49, p. 429–483, doi: 10.2138/rmg.2002.49.8.
- Sutton, S.R., Bertsch, P.M., Newville, M., Rivers, M., Lanzirotti, A., and Eng, P., 2002b, Microfluorescence and Microtomography Analyses of Heterogeneous Earth and Environmental Materials: Reviews in Mineralogy and Geochemistry, v. 49, p. 429–483, doi: 10.2138/rmg.2002.49.8.
- Walker, S.R., Jamieson, H.E., and Rasmussen, P.E., 2011, Application of Synchrotron Microprobe Methods to Solid-Phase Speciation of Metals and Metalloids in House Dust: Environ. Sci. Technol., v. 45, p. 8233–8240, doi: 10.1021/es2008227.
- Warner, J., and Rowson, J., 2007, Technical Report: In-situ Monitoring and Validation of a Uranium Mill Tailings Management Facility Design Using X-ray Absorption Near Edge Structure (XANES) Spectroscopy: Synchrotron Radiation News, v. 20, p. 14–17, doi: 10.1080/08940880701401128.





Figure 2a















## Fe K $\alpha$ - As K $\beta$ - U L $\alpha$



Figure 6

### Fe K $\alpha$ - As K $\beta$ - U L $\alpha$





### Fe K $\alpha$ - As K $\beta$ - U L $\alpha$









