

Characterization of Uranium and Rare Earth Element Mobility Downstream of a Tailings Impoundment Near Bancroft, Ontario

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ABSTRACT

Attenuation of uranium (U) and rare earth elements (REEs) has been observed in stream and wetland sediments, but the geochemical and mineralogical processes involved in sequestering these elements in natural systems are not fully understood. The decommissioned Bicroft Uranium Mine near Bancroft, ON, operated from 1957 to 1963, and processed approximately 2,284,421 tonnes of low-grade, disseminated U ore hosted by pegmatite dykes in amphibolite gneiss. During operations, the mine used two tailings impoundments and a modified stream and wetland system to reduce the concentrations of U, other metals, and radionuclides in tailings effluent to levels below the Provincial Water Quality Objectives. Since mine closure, the streams and wetland have continued to operate as a passive treatment system for tailings effluent, demonstrating the potential viability and longevity of natural attenuation to sequester U and REEs. In this study, we used tangential flow filtration, ICP-ES/MS, scanning electron microscopy, and synchrotron techniques (bulk- and micro-XANES, -XRF, and -XRD) to characterize processes controlling U and REE mobility and attenuation in tailings, sediment, and colloid samples. Results of this study indicate that Fe- and Mn-(oxyhydr)oxides, including goethite [α -FeO(OH)] and birnessite (δ -MnO₂), are the main mineral hosts for U and REEs in colloids and sediments. In addition, detrital grains of U- and REE-bearing minerals were found >200 m downstream in colloids and sediments, showing the potential for long-range transport of colloids and fine particulates in the stream system. While natural attenuation exhibits great potential to reduce U- and REE- concentrations, seasonal influences on the stability of trace metals in sediments were observed and may demonstrate the limitations of streams and wetlands as a viable method of attenuation. The results of this study are intended to aid development of more effective passive treatment systems and improve environmental monitoring strategies for U and REEs.

Keywords: Uranium, rare earth elements, synchrotron micro-analysis, colloids, passive attenuation

INTRODUCTION

The decommissioned Bicroft Uranium Mine is located 19 km southwest of Bancroft, Ontario, Canada in granitic pegmatites (ca. 1020 to 1050 Ma) of the Grenville Geological Province (Evans 1962; Lentz 1996), (Lat. 44°59'30.39"N, Long. 78°2'16.83"W). Since the closure of the mine in 1963, following seven years of operation, the Bicroft site has acted as a passively attenuating stream and wetland system to achieve below-Provincial Water Quality Objectives (PWQOs) for uranium (U) and other trace metals (MOE 2003). The two decommissioned tailings impoundments at the Bicroft Mine, Auger Lake and South Tailings Basin, drain through an approximately 1 km tributary stream and wetland system, to Deer Creek, before being discharged to Paudash Lake where the waters are required to meet PWQOs (MOE 2003). The environmental conditions and geochemical processes that control the mobility of metals and radionuclides at the Bicroft site are poorly understood. Specifically, the methods by which U and rare earth elements (REEs) are released from the tailings basins and then partially sequestered in the stream and wetland system are unknown.

In effluent released from mine tailings, trace metals and other contaminants are generally partitioned between particulate matter, colloids, and dissolved phases. In most studies of natural water systems colloidal material is considered part of the dissolved fraction (<0.45 µm), and any particles unable to pass through a 0.45 µm filter are considered to be suspended particulate matter. Colloids, in aqueous systems, are any suspended material with a single linear dimension between 0.001 µm and 1 µm. Colloids have large surface-area-to-volume ratios due to their small size, which provides increased sites for reactivity and heightened surface charge allowing for high adsorption capacity (Klaine *et al.* 2008). The large surface area of colloidal particles relative to their mass allows for particles to overcome gravitational forces and to remain in suspension in waters of varying velocities, and travel significant distances (1 km to >500 km), until flocculation of colloidal material results from changes in the solution chemistry and the colloids settle from solution (Kersting *et al.* 1999; Kretzschmar and Schäfer 2005; Wigginton *et al.* 2007).

The natural attenuation of U from mine wastes has been observed in other studies of stream and wetland sediments by Schöner *et al.* (2009) in Germany, Veselic *et al.* (2001) in Slovenia, Groudev *et al.* (1999) in Bulgaria, and Lottermoser and Ashley (2005) in Australia. These studies suggest that U is primarily attenuated in Fe- and Mn-oxyhydroxides and natural organic matter; however, the host mineralogy of U was undetermined. The natural attenuation of REEs has been observed in other studies that focused on the use of REEs as a tracer for geochemical processes by relating the absolute and relative concentrations of REEs to a variety of environments (Goldberg *et al.* 1963; Quinn *et al.* 2006). However, the release of lanthanides from mine waste through weathering processes, and their environmental impacts and toxicity once released into aqueous solution, have not been fully characterized. Previous studies have determined that REEs are mobilized under acidic conditions, and precipitated or otherwise sequestered at high pH conditions (Brookins 1989; Verplanck *et al.* 2004). In addition, REEs are known to readily complex with various ligands in the aqueous environment and are often associated with particulate matter and organics in shallow surface waters (Cantrell and Byrne 1987). Critical gaps remain in our knowledge of the host mineralogy and the processes involved in sequestering U and REEs in complex field systems (Brookins 1989; Schöner *et al.* 2009).

This study focuses on understanding the mineralogical and geochemical controls that influence the mobilization, sequestration, and stability of U and REEs (specifically, cerium (Ce) and lanthanum (La)) in sediments of a stream and wetland system sourced by effluent from a U tailings

impoundment at the Bicroft Mine. The passive treatment system has been in operation for over 50 years and thus provides an ideal natural laboratory to study the processes involved in attenuating these trace elements and the long-term effectiveness of this method of pollution control (Parsons *et al.* 2014). Detailed characterization of tailings, colloids, and stream and wetland sediments through field observations, bulk chemistry, and mineralogical observations from scanning electron microscopy and synchrotron micro-analyses were used to identify the main sources for U and REE within the tailings and their attenuation and stability in downstream environments. The results of this study will help to develop better monitoring strategies for U tailings sites and should reduce the impacts of future U and REE mining operations.

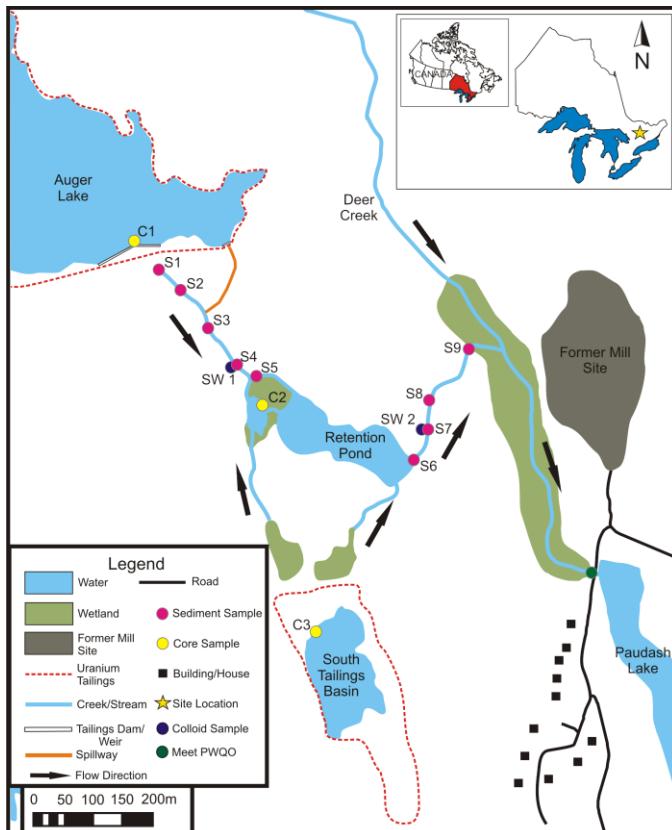


Figure 1 Bicroft Mine site map with field sampling locations of bulk sediment (pink), core (yellow) samples, and surface water (blue) samples. All samples were collected in October 2011, with the exception of a second set of surface water samples in July 2012. PWQOs are to be met at the discharge point of Deer Creek to Paudash Lake (green).

METHODOLOGY

To characterize the chemical and mineralogical controls by which U, La, and Ce are sequestered, 15 bulk samples of hardpan, pebbles, streambed sediments (S1-S9), and tailings were collected in October 2011 from the tributary stream and wetland system, and tailings basins (Figure 1). In addition, two sediment cores were collected in the Auger Lake tailings basin (C1) and Retention Pond (C2) to examine the effect of redox conditions on the mobility and attenuation of U (Figure 1). Surface water sampling was conducted in October 2011 and July 2012 to account for any seasonal changes in water composition. Two water samples were collected in each field season, with a

sample both upstream and downstream of the Retention Pond, identified as SW1 and SW2 respectively, to determine whether this pond was removing colloids from solution. Tangential flow filtration (TFF) was applied to analyze the colloid fraction from the stream waters at the two locations, using a Millipore Prep/Scale Spiral Wound Ultrafiltration Cartridge. Within 48 hours of collection, the water samples were filtered through a 0.557 m^2 (6 ft^2) TFF cartridge with a 10 kdalton ($0.005\text{ }\mu\text{m}$) filter cut off. The <10 kdalton permeate from the TFF system is assumed to represent the dissolved fraction of the sample (Guegon *et al.*, 2002). The retentate, with a size fraction between $0.45\text{ }\mu\text{m}$ and 10 kdaltons, contains the colloid fraction from the water (Guegon *et al.*, 2002). For further information regarding sample collection and preparation please refer to Laidlow (2013).

Bulk chemistry and X-Ray diffraction (XRD)

Ultra-trace analysis for a 43-element suite plus 12 REEs by inductively coupled plasma-mass spectrometry (ICP-MS) (package 1T-MS), following 4-acid digestion, was completed at ACME Analytical Laboratories on all bulk sediments and sub-samples from sediment cores. Additionally, two samples were re-analyzed by inductively coupled plasma-emission spectrometry (ICP-ES) after 4-acid digestion (package 7TD) to determine the percent-level concentrations of manganese (Mn). To identify the major crystalline phases present in the samples, X-ray diffraction (XRD) was completed using the Philips X-Pert diffractometer at Queen's University.

Petrographic analyses and synchrotron micro-analysis

Thin sections were examined optically under the petrographic microscope and characterized using a scanning electron microscope at Queen's University. Two hard X-ray microprobe synchrotron beamlines were used for trace element micro-analysis: X26A at the National Synchrotron Light Source in Upton, New York and Sector 20-ID beamline at the Argonne Photon Source in Argonne, Illinois. Micro X-ray radiation fluorescence (μ XRF) mapping and micro X-ray diffraction (μ XRD) analyses were conducted at both beamlines, and bulk- and micro-X-ray absorption near edge structure (XANES and μ XANES) were conducted at the Sector 20-ID beamline.

RESULTS AND DISCUSSION

Characterization of U and REEs in colloids

During the process of TFF, orange-yellow staining of the ultrafiltration cell was observed for upstream (SW1) water samples. Calculated filter losses are shown in Figure 2. In both the October and July sampling, there were significant losses of iron (Fe) and aluminium (Al), as well as all REEs in the SW1 samples (Figure 2). This demonstrates that these waters were not fully oxidized when sampled and were further oxidized during the filtration process, causing Fe and Al phases to precipitate onto the filter along with their associated REEs.

In Figure 3 it can be seen that U and Mn were present mainly in the dissolved phase, Ce, La, Fe, and Al were present in both the colloidal and dissolved phases, with high proportions of Ce and La in the colloidal phase. This diagram also shows the importance of documenting seasonal variations at sample locations.

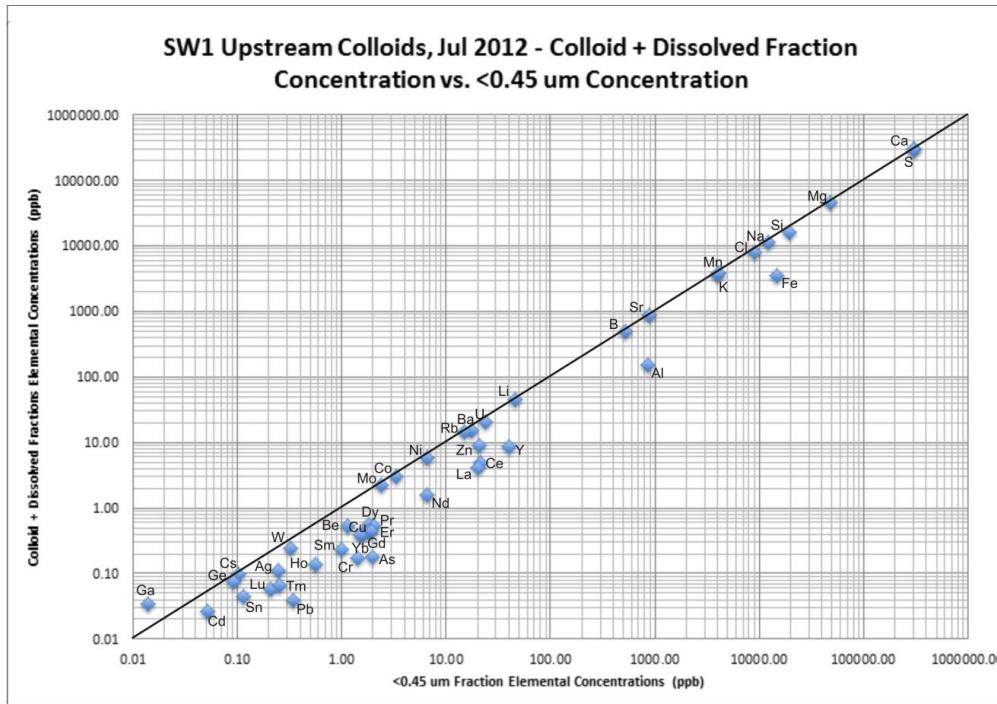


Figure 2 Correlation plot of calculated colloid + dissolved fraction elemental concentrations (ppb) vs. $<0.45 \mu\text{m}$ elemental concentrations (ppb) for SW1 surface water sample from July 2012. Black line represents a 1:1 ratio of concentrations and no element retention on the filter. Elements plotting below the line show greater concentrations in the initial $<0.45 \mu\text{m}$ water sample than in the combined colloid + dissolved aliquots suggesting a loss due to retention on the filter cartridge. Precision is within 5% for most samples, which is represented by the size of each point on the graph.

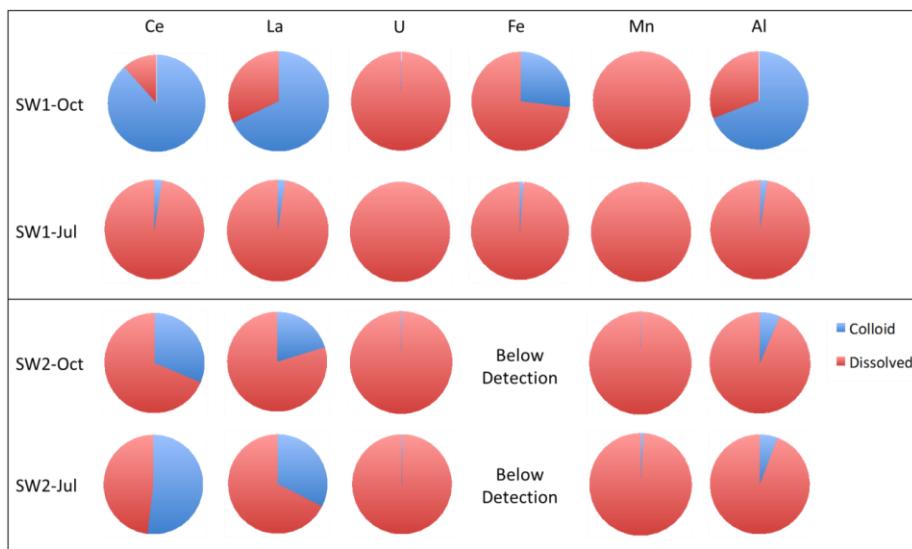


Figure 3 Relative % of Ce, La, U, Fe, Mn, and Al in colloid (blue) and dissolved (red) fractions from TFF.

Lanthanum and Ce were present in both the colloid and dissolved phases, with the greatest relative percent of colloids observed in the SW1-October 2011 sample (Figure 3). Uranium, however, was

predominantly found in the dissolved phase, with less than 1% of its total concentration in the colloid fraction for all samples. This observation is consistent with the results of aqueous speciation modeling by Parsons *et al.* (2014), which demonstrated that >95% of U in the tailings effluent at the Bickerton site occurs as calcium-uranyl-carbonato complexes, which are known to diminish the sorption of U to mineral surfaces and suppress the reduction of U(VI) to the less soluble U(IV).

In the SW1 samples, Al and La showed similar relative percentages in the colloid and dissolved fractions. Concentrations of U and Mn in the dissolved and colloidal fractions showed little variation between the October and July samples. The variance between the SW1 results in October 2011 and July 2012 may be explained in part by dilution of the July 2012 sample by heavy rainfall the day before sampling occurred (Laidlow 2013).

Iron and Mn-oxyhydroxides

Good correlations between Fe and REEs, and Mn and REEs, were observed in the XRF maps (Figure 4), and Fe XANES results suggest a strong association with Fe-oxyhydroxides. At the SW1 (upstream) location, goethite and lepidocrocite dominated the mineralogical composition of the colloids, and at the SW2 (downstream) location, hematite, ferrihydrite and lepidocrocite were the dominant REE-hosting minerals (Figure 5). The observed change in mineralogical composition between SW1 and SW2 may reflect kinetic controls on the formation of Fe-oxyhydroxide minerals in the stream. Hematite is kinetically unlikely to form in solution, but may have formed through dehydration and recrystallization of goethite and ferrihydrite.

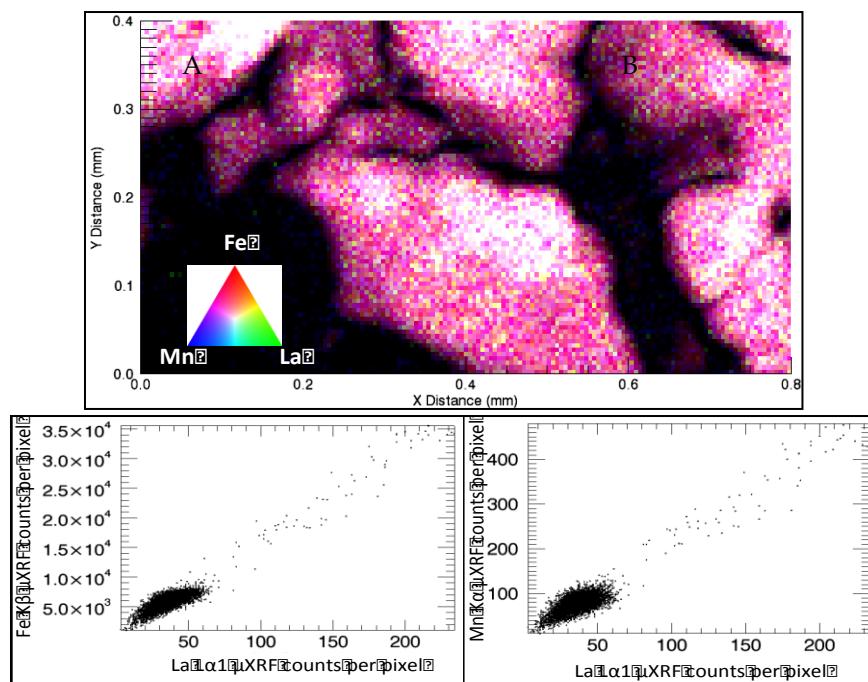


Figure 4 μ XRF element map and associated element correlation plots for REEs on colloid sample SW1 – October 2011. Element counts are directly proportional to element concentrations (Jamieson and Gault, 2012).

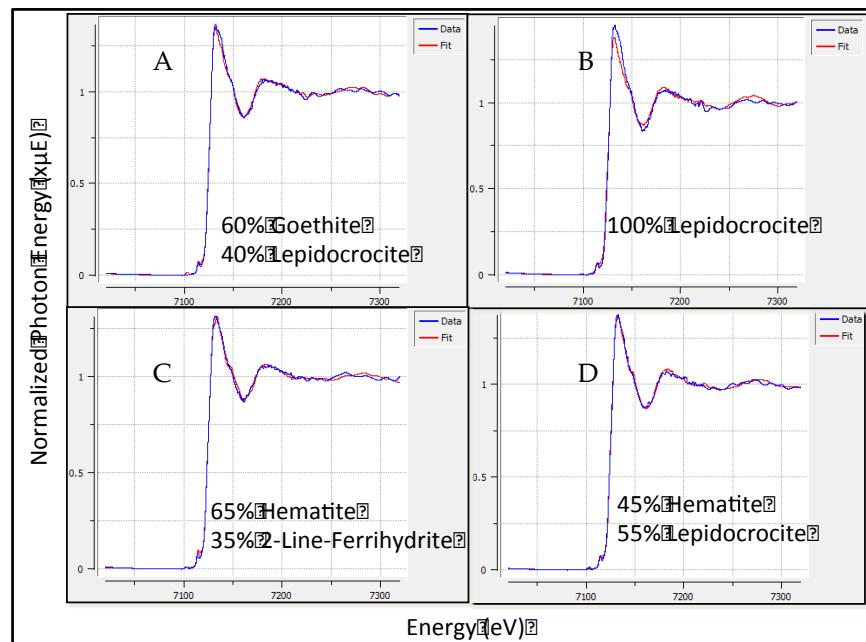


Figure 5 Fitted Fe μ XANES collected from SW1 and SW2 colloid samples from October 2011. Background subtracted Fe μ XANES collected on 2 targets from SW1 (A and B) and 2 targets on SW2 (C and D) were fitted using the standard reference μ XANES patterns for 14 Fe minerals. The blue lines represent the collected, background subtracted scan for the sample and red lines represent the fit of the standard reference scans to the data.

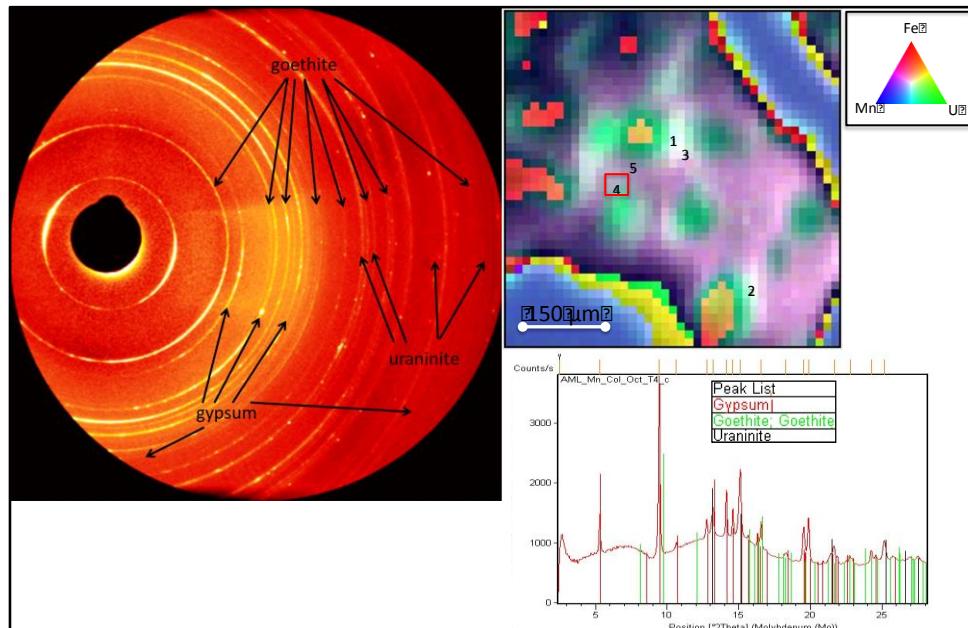


Figure 6 2D μ XRD image showing Debye-Scherrer rings for goethite, gypsum and uraninite and corresponding target location on the tricolor μ XRF map of the SW2 – October 2011 sample. Mixtures of red, blue and green imply a mixture of Fe, Mn and U.

XRF element mapping, in Figure 6, shows a good correlation between Mn and U only at low concentrations. At higher U concentrations, U shows poor correlations with both Fe and Mn,

suggesting that U is primarily hosted by nanoparticulate ore minerals, rather than secondary Fe- and Mn-oxyhydroxides.

Uraninite

Uraninite (UO_2) was identified in the SW2 colloid sample using μ -XRD (Figure 6). This is most likely a detrital phase, as UO_2 is a primary ore mineral in the Bic平安 deposit and is not likely to precipitate from the relatively oxidized tailings effluent. Furthermore, other high-U targets from XRF mapping showed no discernable XRD pattern, but bright spotty images, which are associated with micro-analysis of nano-crystalline particles larger than the spot size of the synchrotron beam. Micro-XANES analyses of colloids with high U and low Fe and Mn concentrations showed that most U was present as U(IV), providing further evidence for detrital U grains in the colloid fraction. This observation is important, as detrital UO_2 transported downstream may oxidize to U(VI) over time, enhancing both the mobility and potential toxicity of this contaminant in the surrounding environment.

Characterization of U and REEs in sediments

Primary grains of UO_2 were identified in the grey, unoxidized section of the tailings core, in sediments downstream in the upper portion of the tributary stream, and in the Retention Pond sediments. The presence of these detrital, nanoparticle-size, grains downstream of the tailings impoundments is important, as they may be a source of further contamination if not maintained in the reduced state. From analysis of the colloids and fine tailings located immediately near the outlet of the tailings dam, it is clear that these UO_2 grains are mobilized from the tailings impoundments and released into the stream and wetland system through effluents.

Generally, most U was present as U(VI) in bulk stream sediments; however both U(IV) and U(VI) were present below the Retention Pond. Variation in the amount of U(IV) and U(VI) present depended on the local mechanism of attenuation. While goethite, maghemite, and lepidocrocite were the predominant Fe-oxyhydroxide minerals observed upstream of the Retention Pond, downstream of the Retention Pond a notable change in the predominant Fe-oxyhydroxide mineralization in stream sediments, to hematite, ferrihydrite and lepidocrocite, was observed. The presence of goethite and lepidocrocite above the Retention Pond is likely related to the relatively rapid precipitation of these phases from tailings pond effluent. Hematite however, is generally formed as a secondary mineral due to the internal rearrangement and dehydration of precipitated goethite, ferrihydrite and lepidocrocite. Uranium adsorbed to these Fe-oxyhydroxides may undergo reduction through dehydration or incorporation into the crystal structure by recrystallization, increasing the relative proportion of U(IV) in these sediments (Marshall *et al.* 2014).

CONCLUSION

The release of U and REEs from U mine wastes into surface waters is of concern for water quality, and the health of humans, organisms, and the surrounding environment. At the Bic平安 Mine, an enhanced natural stream and wetland system has passively attenuated these elements of concern from tailings effluents for over 50 years, and sequestered these contaminants into local stream and wetland sediments. If the sediments and adsorbed species in this stream and wetland system

remain undisturbed, U and REEs sequestered in these sediments could be immobilized for many years. The results of this research have led to the following five main conclusions:

- The release of U, Ce, and La into the tributary stream and wetland system is associated with both oxidative and reductive dissolution of tailings within the impoundments, and subsequent release in mine tailings effluent;
- Colloids in the stream and wetland system are dominantly composed of Fe-oxyhydroxides;
- Detrital grains of UO₂ are present in the colloid fraction above the Retention Pond;
- REE-hosts in stream and wetland sediments are primarily composed of Fe- and Mn-oxyhydroxides, while U is present mainly in the dissolved phase;
- After 50 years, the stream and wetland at the Bicroft Mine continue to be an effective passively attenuating remediation system for effluent from low-grade U mine tailings.

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