Geological Survey of Canada
Scientific Presentation 24

# CONTROLS ON URANIUM, RARE EARTH ELEMENT, AND RADIONUCLIDE MOBILITY AT THE DECOMMISSIONED BICROFT URANIUM MINE, ONTARIO

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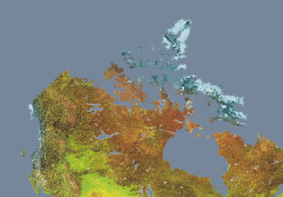
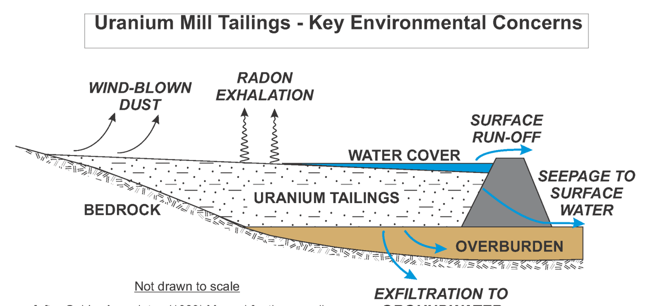


## Abstract

Uranium ores have been mined in Canada since the 1930s, resulting in the production of approximately 214 million tonnes of mill tailings. These tailings may pose a risk to ecosystems and human health because of their long-lived radioactivity, and their potential to release radionuclides, metal(loid)s, radon gas, and milling reagents to the environment. The main objective of this study was to characterize the processes controlling the release, transport, and fate of U, radionuclides (Ra-226, Pb-210), and rare earth elements (REEs) downstream from two decommissioned tailings impoundments at the Bicroft Uranium Mine near Bancroft, Ontario. The Bicroft Mine operated from 1957 to 1963, and milled approximately 2,284,421 tonnes of U ore from granitic pegmatite dykes. This type of U deposit is relatively widespread throughout the Grenville Province in Ontario, Québec, and Labrador, and has recently been the focus of exploration as a source of REEs and other strategic metals. Samples of tailings, sediments, surface waters, and colloids were collected from the Bicroft Mine between 2010 and 2012. Regional-scale sampling of sediments and waters, as well as reanalysis of archived stream and lake sediments, were undertaken to determine natural background variation. The concentration of U in the Bicroft tailings samples varies from 3.1 to 210 mg/kg (median 19 mg/kg). Much higher concentrations were found in stream and pond sediments below the tailings impoundments (54 to 730 mg/kg; median 150 mg/kg). Uranium concentrations in regional lake sediments range from 0.4 to 140 mg/kg (median 4.2 mg/kg), and regional stream sediments range from 1.2 to 110 mg/kg (median 4.6 mg/kg). Seasonal sampling of tailings effluent shows that these waters are circumneutral (pH 6.6–8.3) and that the downstream concentrations of U and Ra-226 are generally highest in the fall. Comparison of filtered and unfiltered effluents, combined with synchrotron microanalyses of colloids, shows that the downstream mobility of REEs is limited by sorption to Fe- and Mn-(oxy)hydroxides. In contrast, U occurs mainly in the dissolved phase and its mobility does not appear to be limited by sorption to colloids or precipitation of secondary U phases. Geochemical modeling of the effluent demonstrates that the aqueous speciation of U is dominated by calcium-uranyl-carbonato complexes [e.g. $Ca_2UO_2(CO_3)_3$], which are known to diminish the sorption of U to mineral surfaces and suppress the reduction of U(VI) to less soluble U(IV). The results of this study provide improved understanding of the long-term stability of U tailings, and have implications for the design of environmental monitoring plans.

## Motivation for Study

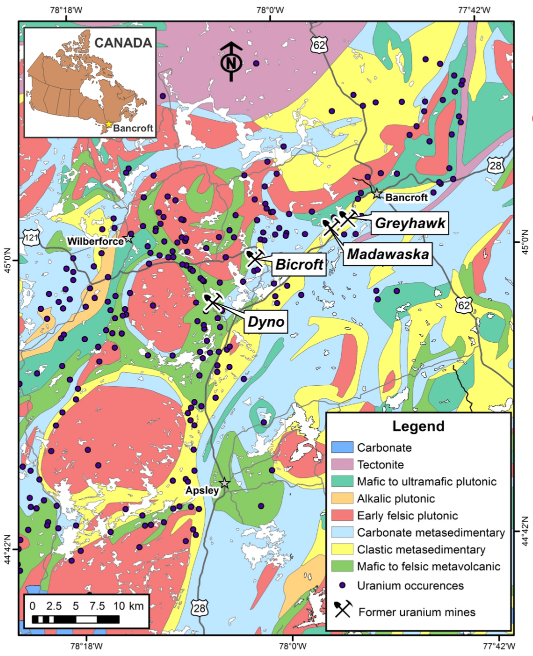
- Global demand for U remains strong, with over 430 nuclear reactors in operation, 70 under construction and dozens at the planning stage.
  - Canada is the world's second-largest U producer (~17% of total output)
- Demand for REEs has increased substantially in recent years in response to new applications (e.g. smartphones, wind power, electric cars) and China's recent REE export quota.
  - Most REE deposits are enriched in Th ± U
- Uranium mining and milling in Canada has produced ~214 million tonnes of tailings.
  - Canadian companies hope to supply at least 20 percent of global demand for REEs by 2018, which will generate additional low-level radioactive mine wastes across the country.




[after Golder Associates (1983) Manual for the sampling of uranium mine tailings. Report 821-1327]

- Uranium mill tailings contain a mixture of crushed ore and gangue minerals, secondary phases, and mill waste solutions. Approximately 85% of the original radioactivity in the U ore is contained in the tailings, including radionuclides such as Pb-210, Th-230, and Ra-226. The tailings may also contain sulphide minerals that can oxidize to produce acidic drainage and release metal(loid)s to the environment.

## U-Th-REE deposits near Bancroft, Ontario




Bedrock geology map of the area surrounding Bancroft, ON, showing the former Bicroft, Dyno, Greyhawk, and Madawaska uranium mines.

[geology from Ontario Geological Survey (1991) Bedrock geology of Ontario, southern sheet; Ontario Geological Survey, Map 2544, scale 1:1,000,000]

- U-Th-REE-bearing granitic pegmatites occur throughout the Grenville Province in Ontario, Québec and Labrador, and are being reappraised for possible U and REE mining.
- Uranium mining has taken place at three sites near Bancroft:
  - Faraday-Madawaska Mine (4,673,260 tonnes milled; 1957-64; 77-81)
  - Bicroft Mine (2,284,421 tonnes milled; 1957-1963)
  - Dyno Mine (743,127 tonnes milled; 1958-1960)
- U, Th, and REEs were produced from various minerals, including uraninite [$UO_2$], uranothorite [$(Th,U)SiO_4$], thorite [$ThSiO_4$], uranophane [$Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$], and allanite [$(Ce,Ca,Y,La)_2(Al,Fe)_3(SiO_4)_3(OH)$].
- Ore processing included leaching at pH 1.9 with sulphuric acid, ion exchange, and precipitation to form yellowcake.
  - Tailings neutralized to pH 8.0 with $Ca(OH)_2$ before disposal

Dyno Mine headframe (*c.* 1959)
[Archives of Ontario, RG 13-130-1-223.1, A0 3868]

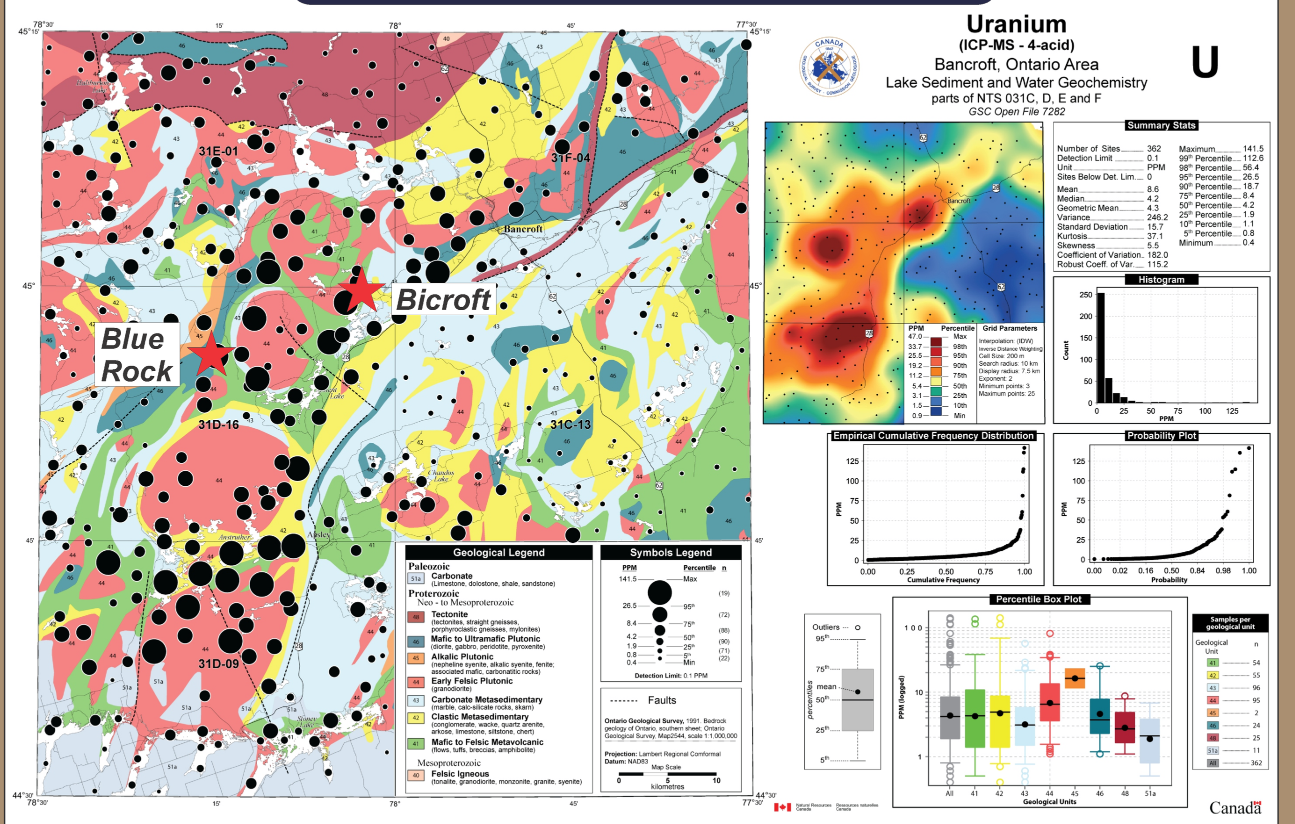
Bicroft 1000 ton-per-day mill (1956)
[Archives of Ontario, RG 13-130-1-223.2, A0 3867]

## Objectives of Study

1. Characterize regional background of U, Th, and REEs in sediments and surface waters.
2. Assess the controls on metal, radionuclide, and REE mobility in U tailings effluent.
3. Examine the role of secondary minerals and colloids in transport of U and REEs.

**The overall goal of this research is to characterize the environmental risks associated with U-Th-REE granite pegmatite deposits to better inform public policy and regulatory decision-making.**

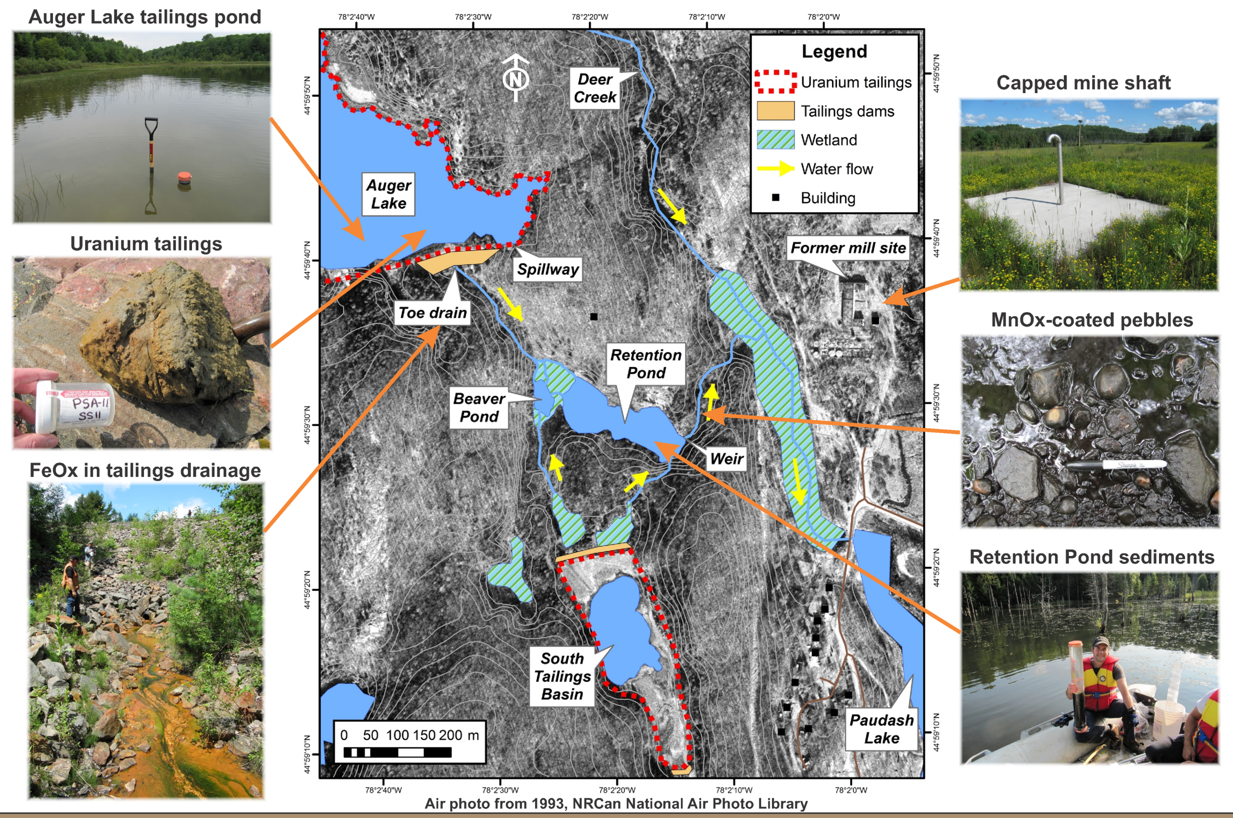
## Regional Background Sampling




Total U in lake sediments near Bancroft, ON, based on re-analysis of 362 samples collected by the GSC in 1976 and 1982

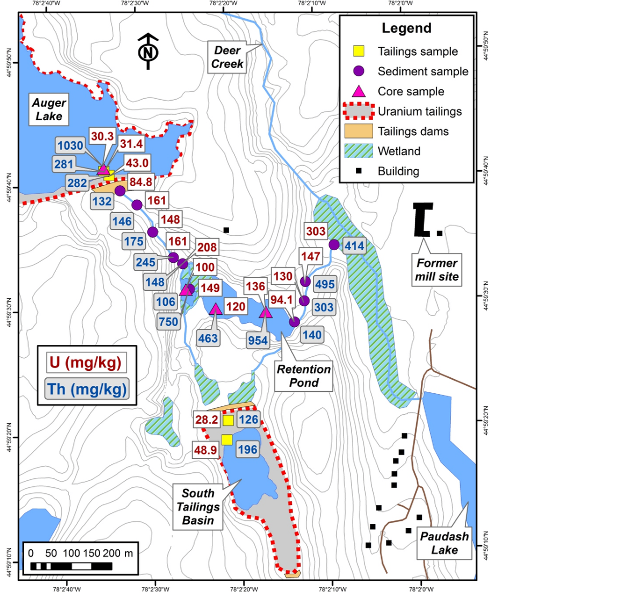
- Uranium concentrations in regional lake sediments range from 0.4 to 140 mg/kg (median 4.2 mg/kg), and regional stream sediments range from 1.2 to 110 mg/kg (median 4.6 mg/kg).
  - Concentrations are highest around the margins of granite plutons, and lowest over carbonate terrain.
  - Recent sampling in 2010-2012 showed that the highest U concentrations (up to 1300 mg/kg) were measured near mineralized, but unmined areas in the vicinity of the Blue Rock U-REE-Th occurrence.

## Bicroft Uranium Mine: Site Overview

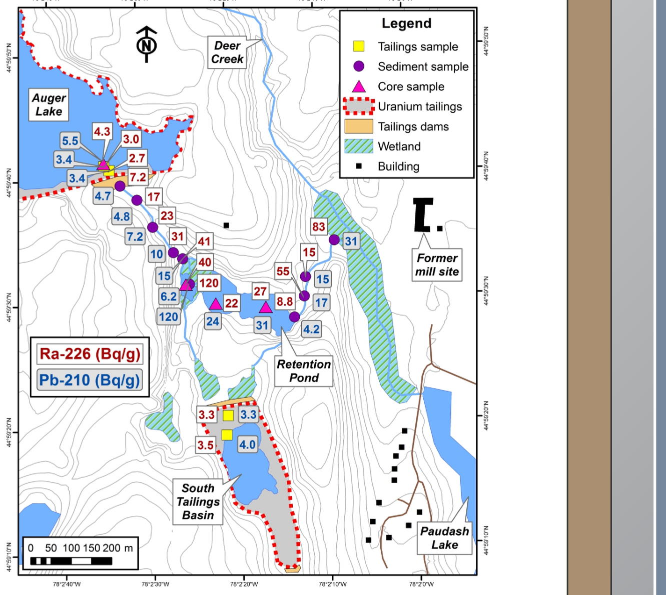



Air photo from 1993, NRCan National Air Photo Library

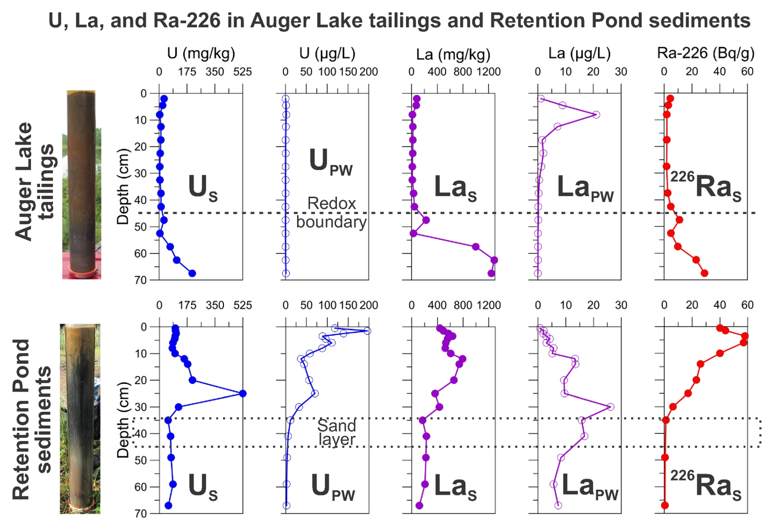
## Metals & Radionuclides in Tailings & Sediments

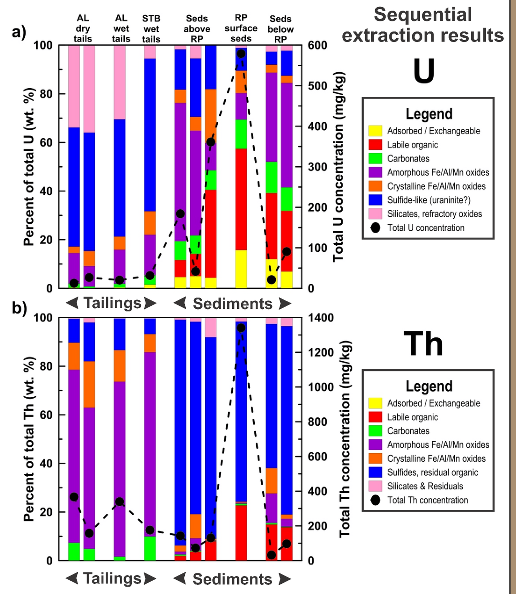



U and Th concentrations (mg/kg) in sediments and tailings collected at the Bicroft Uranium Mine in 2011 and 2012



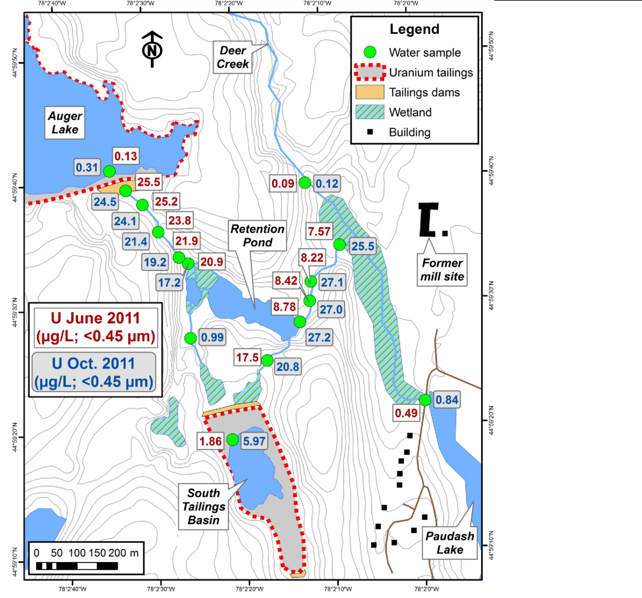

Ra-226 and Pb-210 concentrations (Bq/g) in sediments and tailings collected at the Bicroft Uranium Mine in 2011 and 2012



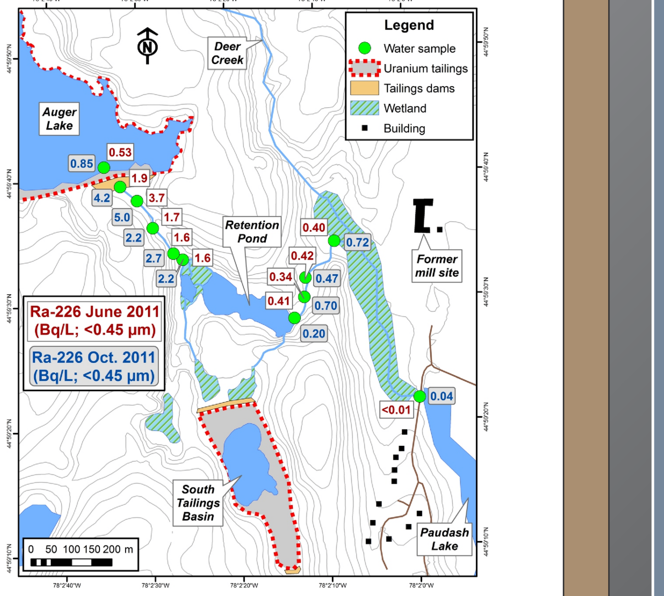




- Solid-phase concentrations of U, Th, REEs, and radionuclides are highest in stream sediments below the tailings impoundments, as a result of scavenging by secondary Fe- and Mn-oxide precipitates.
- Synchrotron-based micro-mineralogical analyses show that goethite (α-FeOOH) and birnessite (δ-$MnO_2$) are the main mineral hosts for U and REEs in the stream sediments, in addition to detrital ore minerals.
- Sequential extraction data show that in the Retention Pond sediments, most U is associated with relatively labile adsorbed and organic phases, which may enhance the mobility of U in pore waters.

## Metals & Radionuclides in Surface Waters



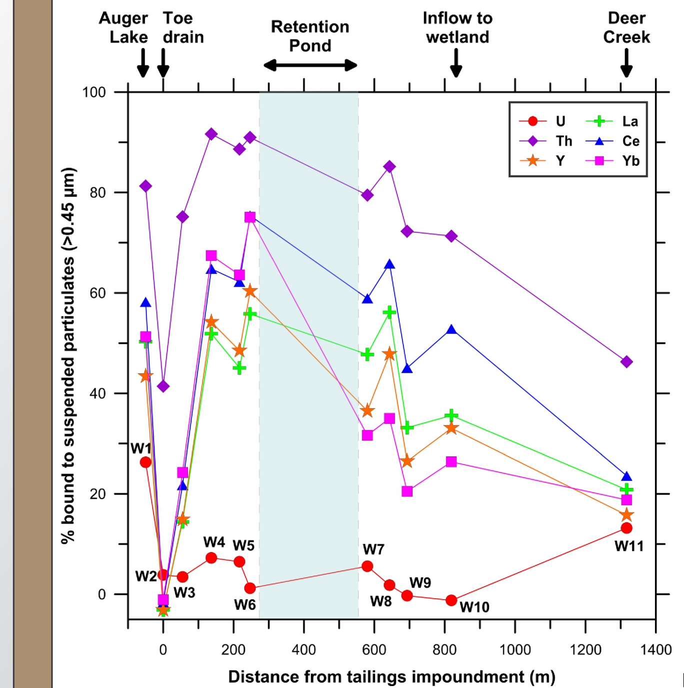

Uranium concentrations (μg/L) in filtered surface water in June and October 2011



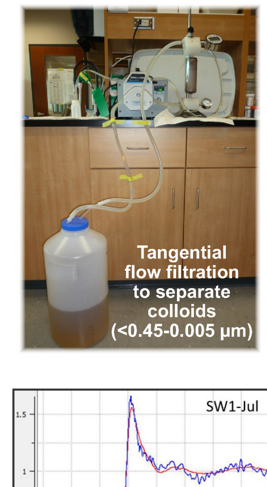

Radium-226 concentrations (Bq/L) in filtered surface water in June and October 2011

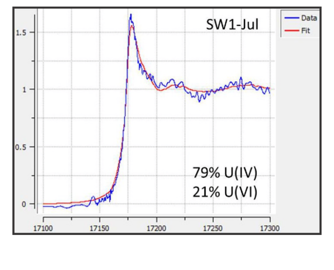
- Effluent from the Bicroft tailings is circumneutral (pH 6.6–8.3) and has high concentrations of Ca and $SO_4$.
- The Retention Pond is an effective sink for Fe, Mn, and other particle-reactive elements (e.g. REEs) in the tailings effluent. However, U and bicarbonate concentrations *increase* below the pond in the fall, suggesting that the pond sediments may serve as a source for these elements under some conditions.

## Controls on U, Th, REE & Radionuclide Mobility



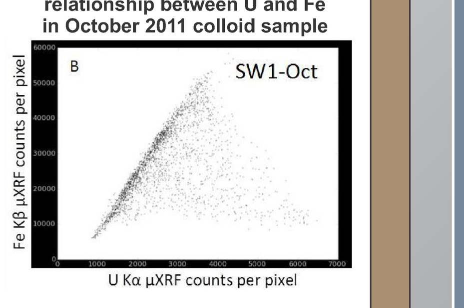

Percentage of U, Th, Y, La, Ce, and Yb bound to suspended particulates (>0.45 μm) in Bicroft surface waters, June 2011.

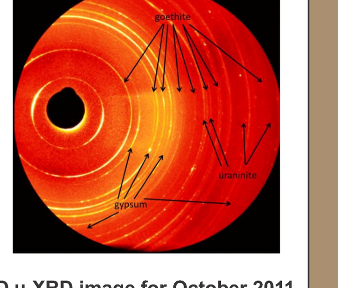



Bulk U XANES spectrum for July 2012 colloid sample showing a mix of 79% U(IV) and 21% U(VI)

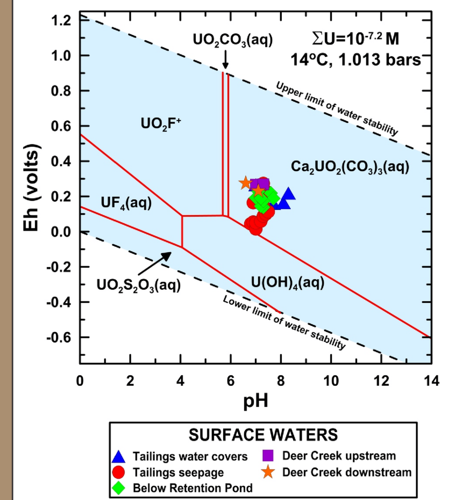
μ-XRF correlation plot showing relationship between U and Fe in October 2011 colloid sample



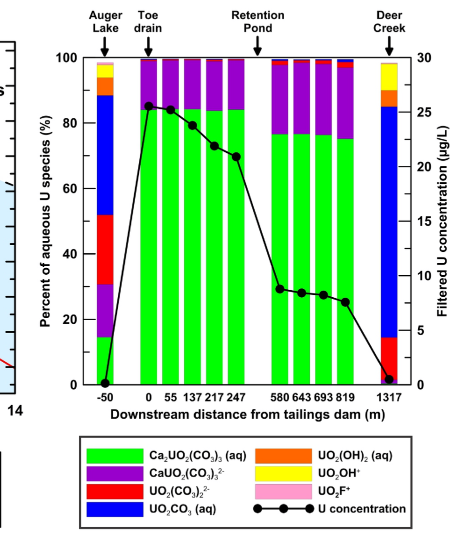



2D μ-XRD image for October 2011 colloid sample showing a mix of goethite, gypsum, and uraninite

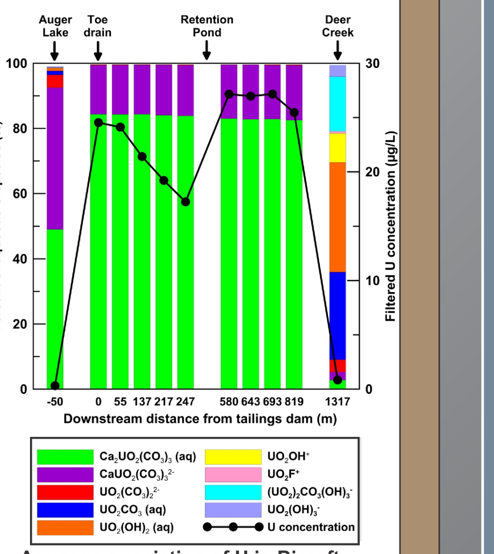
- Comparison of element concentrations in filtered (0.45 μm) and unfiltered surface waters shows that Th and REEs partition strongly to suspended particulates as effluent from the Auger Lake tailings dam is progressively oxidized. In contrast, most U in the tailings effluent is *not* bound to suspended material.
- Analyses of colloid samples using synchrotron-based X-ray absorption near edge structure (XANES) shows that U occurs in both oxidized [U(VI)] and reduced [U(IV)] forms. Micro-X-ray fluorescence (μ-XRF), and micro-X-ray diffraction (μ-XRD) measurements confirm that U in the colloids is hosted by a mix of detrital ore minerals (e.g. uraninite) containing U(IV), and Fe- and Mn-(oxy)hydroxides with adsorbed U(VI).




Eh-pH diagram showing predominance fields for aqueous U species in Bicroft surface waters




Aqueous speciation of U in Bicroft surface waters in June 2011



Aqueous speciation of U in Bicroft surface waters in October 2011

- Aqueous speciation modeling demonstrates that >95% of U in the tailings effluent 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 less soluble U(IV). Increased bicarbonate concentrations in the Retention Pond in October lead to a greater proportion of U as $Ca_2UO_2(CO_3)_3$ (aq), which may contribute to the enhanced U mobility observed in the fall.

## Conclusions

- Uranium concentrations in regional lake sediments are highest around the margins of granite plutons, and lowest over carbonate terrain. The highest values are found in mineralized, but unmined areas.
- Iron- and Mn-(oxy)hydroxides and detrital ore minerals are the main hosts for U, Th, and REEs in colloids and stream sediments. In the Retention Pond, U is hosted mainly by labile organic matter.
- Seasonal sampling of tailings effluent at the Bicroft Mine in 2011 shows that the concentrations of U and Ra-226 downstream of the Retention Pond are generally lower in the summer than in the fall.
- Passive treatment of tailings effluent in the Retention Pond leads to a decrease in the concentrations of most elements, but the pond sediments now serve as a long-term source of U to the environment.

## Acknowledgements & Contact Information

This study was undertaken as part of the Environmental Geoscience Program, Earth Sciences Sector, Natural Resources Canada. We wish to thank Bill LeBlanc, Alain Grenier, and Rick McNeil of the GSC and Tyler Nash and Bart Warren of Queen's University for their expert assistance in the field. Judy Vaive and Pierre Pelchat of GSC-Ottawa are gratefully acknowledged for performing all water analyses and sequential extractions. Historical images of the Dyno Mine and Bicroft Mine are reproduced with permission from the Archives of Ontario. Tony Lanzirotti and Sue Wirick are thanked for their guidance with analyses at Beamline X26A, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Thanks to Robert Gordon for his assistance with analyses at the Sector 20-ID Beamline, Advanced Photon Source, Argonne National Laboratory. Lac Properties Inc. (c/o Barrick Gold Corporation) and Dave Rey are graciously acknowledged for allowing us to access the Bicroft Mine site and collect samples for this research. This poster was prepared for presentation at the Atlantic Geoscience Society Colloquium, Wolfville, NS, February 2014, and has not been subject to the normal editorial process that precedes formal publication. Further information about this study may be obtained from Dr. Michael Parsons at the Geological Survey of Canada (Atlantic), Natural Resources Canada, P.O. Box 1006, Dartmouth, Nova Scotia B2Y 4A2; Phone: (902) 426-7363; Fax: (902) 426-4104; E-mail: Michael.Parsons@NRCan.gc.ca.

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2014

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doi:10.4095/293623
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Presented at the 40th Atlantic Geoscience Society Colloquium and Annual Meeting, Wolfville, Nova Scotia
Date presented: February 2014

Recommended citation
Parsons, M.B., Friske, P.W.B., Laidlow, A.M., and Jamieson, H.E., 2014. Controls on uranium, rare earth element, and radionuclide mobility at the decommissioned Bicroft Uranium Mine, Ontario; Geological Survey of Canada, Scientific Presentation 24, poster. doi:10.4095/293623