Natural Resources Canada
Ressources naturelles Canada

GEOLOGICAL SURVEY OF CANADA
OPEN FILE 7992

Groundwater Chemistry of Uranium-Thorium-Rare Earth Element Deposits, Bancroft Area, Ontario

A.J. Desbarats and J.B. Percival

2016

GEOLOGICAL SURVEY OF CANADA
OPEN FILE 7992

Groundwater Chemistry of Uranium-Thorium-Rare Earth Element Deposits, Bancroft Area, Ontario

A.J. Desbarats and J.B. Percival

2016

doi:10.4095/297779

Recommended citation
Desbarats, A.J. and Percival, J.B., 2016. Groundwater Chemistry of Uranium-Thorium-Rare Earth Element Deposits, Bancroft Area, Ontario; Geological Survey of Canada, Open File 7992, 1 .zip file. doi:10.4095/297779

Cover photograph: Head frame of the Amalgamated Rare Earth No.2 mine in 1956. From Satterly (1957).
© Queen's Printer for Ontario, 1957. Reproduced with permission.

FOREWORD

Environmental geoscience for responsible resource development is a strategic priority of Natural Resources Canada (NRCan). The department’s objectives with respect to this priority are to provide authoritative geoscience information to all stakeholders in order to reduce environmental risks associated with mineral resource development and to improve the efficiency of the regulatory process. In support of NRCan objectives, the Geological Survey of Canada (GSC) undertook a project entitled “Environmental Impact Assessment Tools for Metal Mines” during the 2009-2014 cycle of the Environmental Geosciences Program of the Earth Sciences Sector (ESS). The project objectives were to generate geoscience data and knowledge supporting federal initiatives related to environmental impact assessments, and to develop methods that reduce the uncertainty and increase the relevance of environmental risk characterization studies for new mine developments. The project’s desired outcome was to ensure that potential environmental impacts from the development of mineral resources are determined based on sound geoscience evidence. Field and laboratory studies conducted under this project focused on regions and sites that were known to present potential risks to human and environmental health or to require risk-management plans relying on geoscience knowledge. One of the regions selected for study was the historical Bancroft uranium mining camp in southeastern Ontario. This report presents an investigation of groundwater quality at sites of past exploration and mining activity in the Bancroft area. The results herein will help ensure that environmental assessments better anticipate potential impacts to groundwater quality from new mining developments in similar geological settings in Ontario and elsewhere.

SUMMARY

Granitic pegmatite-hosted U-Th-REE deposits and related mineralized skarns and calcite dikes are widespread within the Grenville geological province of eastern Canada, although mining of these deposits has been limited to the Bancroft area of Ontario. Renewed exploration for this type of mineral deposit in Ontario and Québec has raised concerns about possible impacts to groundwater quality. In order to better inform public debate on uranium exploration, government policy, and regulatory decision-making, the Geological Survey of Canada (GSC) has undertaken a study of groundwater quality at ten historical mines and prospects in the Bancroft area focusing on trace elements of potential environmental concern. Groundwater samples were obtained from flooded shafts, flowing adits and diamond drill holes.

Uranium, from the oxidation and dissolution of uraninite and uranothorite, occurs at concentrations as high as 2580 µg/L. The Health Canada (2014) Maximum Acceptable Concentration (MAC) of 20 µg/L was exceeded in approximately 70% of samples. It was found that groundwaters exhibiting U concentrations less than the MAC are unlikely to exhibit radium-226 and lead-210 radionuclide activities in excess of regulatory limits which are 0.5 and 0.2 Bq/L, respectively. The high mobility of U in shallow oxic groundwaters can be attributed to the availability of dissolved Ca and carbonate species for the formation of stable aqueous complexes known to inhibit adsorption. Because of its high mobility in shallow groundwater systems, U may pose an environmental risk where mine adits drain to nearby surface water receptors. This was found to be the case at the Amalgamated Rare Earth No.2 mine.

Thorium is released concurrently with U from the oxidation and dissolution of thorian uraninite and uranothorite. However, Th concentrations are very low with a maximum of only 11 µg/L in unfiltered groundwater samples. Almost all Th is removed from solution close to source.

Allanite is the most likely source of Light Rare Earth Elements (La-Gd) whereas sources of Heavy Rare Earth Elements (Tb-Lu) appear to be dispersed among numerous minerals. A maximum total REE concentration of 126 µg/L was observed in unfiltered groundwater samples.

It was found that the ranges of Th, LREE and HREE concentrations observed in this study fall within the ranges observed in groundwaters from unmineralized Precambrian bedrock although mean concentrations are somewhat higher. Uranium concentrations in groundwater from U-Th-REE deposits exhibit a much wider range than background values and their mean is more than 50 times greater. The MAC for uranium (20 µg/L) provides a reasonable threshold for distinguishing groundwaters in contact with U-Th-REE deposits from the natural background.

This retrospective investigation of groundwater quality at historical mine sites in the Bancroft district provides geoscience data and knowledge useful for the environmental assessment of new mining projects in similar geological settings. This information can be used to anticipate potential environmental impacts associated with future resource development and to plan appropriate mitigation measures accordingly.

TABLE OF CONTENTS

INTRODUCTION

Background

With renewed consideration of nuclear power generation as a means of reducing greenhouse gas emissions, there has been a corresponding resurgence in uranium exploration across Canada. However, moratoria are currently in place in British Columbia, Nova Scotia, and Québec. Recent controversies over uranium exploration activities in eastern Ontario, western Québec and the Québec lower north shore highlight public concern about environmental risks associated with uranium resource development. The controversies surrounded the development of small granitic pegmatite-hosted uranium-thorium-rare earth element (U-Th-REE) deposits (Rogers et al., 1978), a sub-economic class of mineralization widespread within the Grenville geological province of eastern Canada, including parts of Ontario, Québec and Labrador (Lentz, 1991). To date, however, actual mining of such deposits has only taken place in the Bancroft area of Ontario. Because these deposits are found relatively close to population centres of southern Canada, the perception of risk associated with their development may be more acute. In order to better inform public debate on uranium exploration, government policy, and regulatory decision-making, an authoritative geoscience-based characterization of environmental risks from this class of deposit is required. A retrospective investigation of environmental impacts from historical mining activity in the Bancroft district provides a means of acquiring relevant geoscience knowledge useful to regulators and proponents of new mining projects in similar geological settings. This knowledge can help anticipate and mitigate environmental impacts associated with future mine developments.

History of Uranium Mining in the Bancroft District

Exploration for radioactive minerals in the Bancroft district occurred in three distinct phases (Satterly, 1957; Proulx, 1997). The first exploration phase was spurred by financial incentives contained in the Radium Act of 1914 and led to the discovery of radium ore (uraninite) by W.M. Richardson in 1922 (Proulx, 1997). Development of the Richardson property by the Ontario Radium Corporation, and later by International Radium and Resources Limited, included underground work and the construction of a mill. Following unsuccessful milling trials, operations on the property ceased in 1933. Another discovery led to the incorporation of Canada Radium Mines Limited in 1926. Operations on that property started in 1932 and included excavation of a 122 m shaft, lateral development on three levels, and construction of a mill. Operations ceased in 1942 after unsuccessful test milling of the ore.

A brief second phase of exploration occurred between 1947 and 1951. This coincided with the establishment in 1947 of a guaranteed minimum price for uranium concentrate by the Government of Canada through its agent Eldorado Mining and Refining Limited (Proulx, 1997). During that period, the Richardson property was further explored by Fission Mines Limited and underground development work was carried out by Cardiff Mines Limited and the Rare Earth Mining Corporation of Canada on their respective properties.

The third phase of exploration started in 1953 when the United States Atomic Energy Commission agreed to purchase all the uranium concentrate that Canada could produce. The purchases were based on special price contracts negotiated by Eldorado Mining and Refining Limited with individual producers and guaranteed until 1962 (Proulx, 1997). At around the same time, a large-scale airborne radiometric survey revealed numerous radioactive anomalies in the Bancroft area. This combination of circumstances led to a two-year staking rush and the start of the Bancroft uranium boom (Proulx, 1997). By 1956, exploration work had been conducted on 125 properties in the area (Satterly, 1957) although only four of these properties were ever developed into producing mines. The Bicroft mine was the first to open in 1956 but closed in 1963. The Faraday and Greyhawk mines opened in 1957 and closed in 1964 and 1959, respectively. The Canadian Dyno mine opened in 1958 and closed in 1960. Under new ownership, the Faraday mine reopened as the Madawaska mine between 1976 and 1982. Production summaries and reserve estimates for these mines and for selected advanced prospects are presented in Table 1. Photographs of two historical mine properties are shown in Figure 1.

Since the end of most mining activity in the 1960s, there has been sporadic exploration in the Bancroft area coinciding with spikes in the price of uranium. Most recently, there was a minor surge in exploration between 2005 and 2007 during which diamond drilling was conducted on some of the old prospects including the Halo, Amalgamated Rare Earth No. 2 and Northern Nuclear properties. Although exploratory activity rapidly subsided, it raised public awareness of uranium mining and concerns about its environmental legacy in the Bancroft district.

Risks to Groundwater Quality

Impacts to groundwater quality have emerged as the uppermost public concern related to uranium exploration since groundwater is the sole source of potable supply for most rural inhabitants. Risks to groundwater quality from uranium deposits in their undisturbed state are caused by geochemical interactions between groundwater and host rocks which may release dissolved contaminants including metals and radionuclides. Generally, these risks are localized in the immediate vicinity of the deposits (Chamberlain, 1964). Mining activities, however, can significantly enhance geochemical reactions and the mobilization of contaminants (Campbell et al., 2015). This is because mine openings, excavation-related fracturing, and dispersal of fine-grained ore particles within the workings increase the surface area of reaction between groundwater and contaminant-bearing minerals. Discharge of this impacted groundwater from flooded mine workings may then affect surface water quality directly. The principal contaminants of concern associated with the granitic pegmatite-hosted U-Th-REE deposits of the Bancroft district are uranium (U), Thorium (Th), and their radioactive decay products. Rare Earth Elements (REE) may also be mobilized by mining this class of deposit.

Table 1: Uranium production and ore reserve estimates for Bancroft District past-producing mines and prospects. For past-producers, reserve estimates are at the time of closure. Reserve estimates are based on historical sources and are not NI-43-101 compliant.

Mine or Prospect	Production (tonnes)	Production Grade (% U_3O_8)	Reserves (tonnes)	Reserves Grade (% U_3O_8)	Reference*
Madawaska (Faraday)	4,536,187	0.099	758,583	0.151	1
Bicroft	2,333,106	0.086	507,125	0.100	2
Canadian Dyno	599,523	0.060	453,600	0.065	3
Greyhawk	73,054	0.069	181,400	0.065	2
Halo	-	-	428,198	0.112	2
Rare Earth #1	-	-	196,554	0.110	2
Rare Earth #2	-	-	265,305	0.095	2
Croft	-	-	888,884	0.060	2
Kenmac Chibougamau	-	-	181,440	0.200	2

*References: 1: Alexander (1986); 2: Gordon et al. (1981); 3: Griffith (1986)

Uranium concentrations in groundwater are highly variable and depend on a number of factors including bedrock geology, the availability of U-bearing minerals, geochemical conditions and the groundwater flow system. Uranium may be particularly concentrated in felsic igneous rocks, such as granites and granitic pegmatites, formed in late stages of magma crystallization. Because of its large ionic radius and high valence state, U is excluded from the crystal structure of minerals formed in earlier mafic stages of crystallization. Uranium is preferentially incorporated into the crystal structure of late-forming constituent minerals of granitic rocks such as feldspars and micas. In the ore deposits of the Bancroft district, U is also concentrated in minerals such as uraninite, uranothorite, euxenite and betafite. The uranium found in groundwater associated with these deposits results from the slow dissolution of these minerals under oxic conditions that favour uranium mobility.

a)

b)

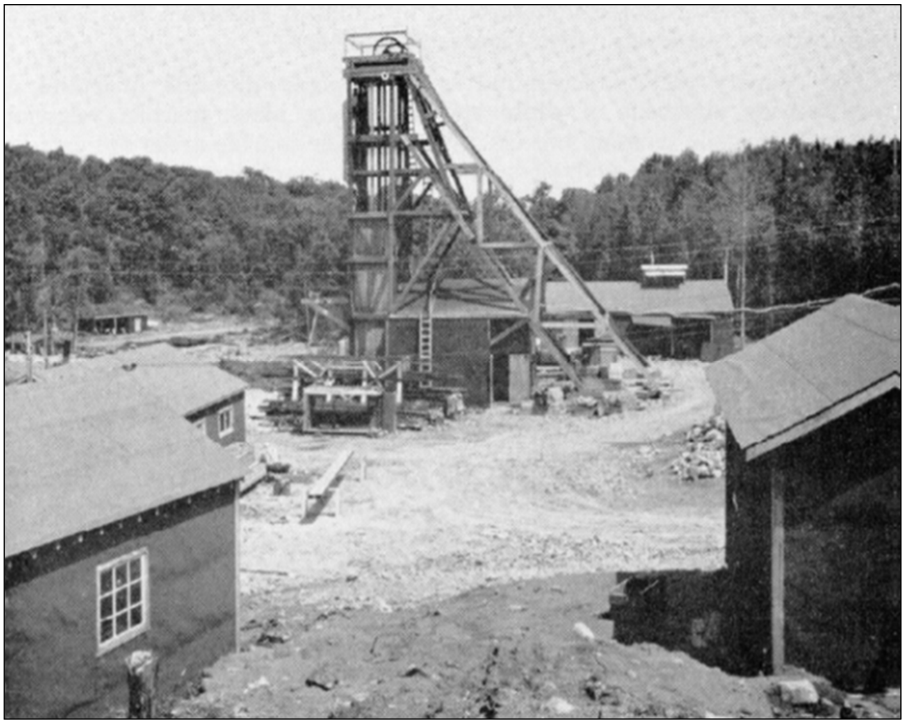

Figure 1: (a) Head frame and buildings of the Canada Radium Mine circa 1942; **(b)** Head frame of the Amalgamated Rare Earth No. 1 Mine in 1956. From Satterly (1957). © Queen's Printer for Ontario,1957. Reproduced with permission.

Naturally occurring uranium is a radioactive heavy metal composed of three isotopes, ^{238}U (99.27 %), ^{235}U (0.72 %), and ^{234}U (0.01 %). These radionuclides decay very slowly and have half-lives ranging from millions (^{234}U) to billions (^{238}U) of years. As a result of these long half-lives, the radioactivity of natural uranium is low. Potential health effects associated with uranium relate less to its radioactivity than to its chemical toxicity as a heavy metal (Health Canada, 2014). Most uranium ingested in drinking water is eliminated from the body. However, a small amount is absorbed and carried through the bloodstream. Once in the bloodstream, uranium compounds are filtered by the kidneys, where they can cause damage to kidney cells (Health Canada, 2014). The maximum acceptable concentration (MAC) of uranium in drinking water in Health Canada's *Guidelines for Canadian Drinking Water Quality* is 0.02 mg/L (Health Canada, 2014). The water quality guideline for the protection of freshwater aquatic life is 0.015 mg/L for long-term exposure (CCME, 2011).

The radioactive decay of ^{238}U, the main constituent of natural uranium, produces daughter products which may also represent environmental concerns. Of these products, the radionuclides radium-226 (^{226}Ra), lead-210 (^{210}Pb) and radon-222 (^{222}Rn) with half- lives of 1620 years, 22 years, and 3.8 days, respectively, pose the greatest potential hazard to human health. Both ^{226}Ra and ^{210}Pb are absorbed in the gastrointestinal track and are associated with increased risks of leukaemia and cancers of the lung, breast, thyroid, bone, digestive organs and skin (Health Canada, 2014). Maximum acceptable concentrations of ^{226}Ra and ^{210}Pb in drinking water are 0.5 and 0.2 Bq/L, respectively (Health Canada, 2014). Metal Mine Effluent Regulations (MMER) standards for ^{226}Ra are 0.37 Bq/L and 0.74 Bq/L for monthly mean and maximum authorized concentrations, respectively (MMER, 2002). Radon-222 is a gas, highly soluble in groundwater, and linked to an increased risk of lung cancer if inhaled. However, because of its high volatility it presents a negligible health risk from ingestion and no maximum acceptable concentration in drinking water is required (Health Canada, 2014). If the concentration of ^{222}Rn in the groundwater supply exceeds 2000 Bq/L treatment is recommended in order reduce its release to indoor air (Health Canada, 2014).

In the study area, Th is found mainly in uranothorite and in uraninite. Naturally occurring Th is a radioactive heavy metal composed mainly of the isotope ^{232}Th (99%). This isotope has a 14 billion year half-life and therefore a very slow decay rate. Decay products of thorium-232 include radium-228 (^{228}Ra) and radium-224 (^{224}Ra) with half-lives of 5.75 years and 3.64 days, respectively. Thorium-232 is extremely insoluble (Cothern and Rebers, 1990) and is not readily mobilized in groundwater. Because of its relatively short half-life compared to groundwater travel times and the insolubility of its parent, ^{228}Ra is not readily dispersed far from its source. Radium-224 is a decay product of ^{228}Ra and their concentrations in groundwater tend to be well-correlated (Focazio et al., 2001). Most Th ingested through drinking water is rapidly excreted from the body. However, the remaining amount may accumulate in the bones and pose a risk for bone cancer. The health effects for short- and long-term exposure of humans to drinking water containing specific levels of Th are not well known. A full discussion of risks to human health from Th is presented in a report by the United States Agency for Toxic Substances and Disease Registry (ATSDR, 1990). There are currently no drinking water standards for Th.

Although the health risks from REE in drinking water are not yet well understood (EPA, 2012; Pagano et al., 2015), REE are also of interest here because Bancroft area U-Th-REE deposits provide a useful proxy for as-yet unmined peralkaline rock REE deposits in more remote parts of Canada (Richardson and Birkett, 1996).

Previous Studies

Chamberlain (1964) presented results of a large-scale survey of U hydrogeochemistry covering 2,000 square miles in the Bancroft-Haliburton region. The objective of the survey was to assess hydrogeochemical methods for U exploration in terrain typical of the Canadian Shield. The survey consisted of over 1,100 water samples mainly from lakes, streams and swamps, as well as 76 samples from special localities such as mine workings, open pits and tailings ponds. It was found that anomalous U concentrations in waters associated with mining activity generally decreased to near-background values within a few hundred feet. Uranium removal from solution was attributed to reductive precipitation promoted by decaying organic matter in surface water drainages. More recent multi-element surveys of lake sediment and surface water chemistry in the Bancroft area have been presented by Lund et al. (1984) and Hornbrook et al. (1984).

As part of the broader geoenvironmental characterization of Bancroft area granitic pegmatite U-Th-REE deposits carried out within this GSC project, McNeil and Friske (2014) reported on additional lake sediment data. Grunsky et al. (2014) presented a multivariate statistical analysis of the lake sediment geochemistry data aimed at distinguishing anomalous mineralized zones from regional background. Parsons et al. (2014) and Laidlow et al. (2015) investigated the mobility of U, radionuclides and REE in surface drainage downstream of the Bicroft Mine tailings impoundment. Desbarats et al. (2016) presented a more in-depth analysis of data in this report, focusing specifically on U, ^{226}Ra, ^{210}Pb, Th, and REE in groundwaters associated with mineral deposits. The authors assessed the geological and mineralogical factors as well as the geochemical processes that control the mobility of these trace elements in the groundwater environment.

Objectives and Scope

This study examines the geochemical signature of granitic pegmatite-hosted U-Th-REE deposits in groundwater. Its objectives are to address the following questions:

1. What is the baseline trace element signature of U-Th-REE mineralization in groundwater at a regional scale with reference to bedrock geology?

2. What is the trace element signature of U-Th-REE deposits in drainage from historical exploration prospects and past-producing mines?

3. What geochemical criteria can be used to identify impacts to groundwater from U-Th-REE resource development?

4. What are the geological factors and the geochemical processes that control the release and mobility of species of interest in the mine environment and in the surrounding groundwater flow system?

Groundwater sampling was conducted at 10 field sites including a former producing mine, seven advanced prospects with underground development, and two properties with limited exploration drilling. This study did not investigate groundwater quality associated with the three historical mine tailings storage facilities in the area (Bicroft, Madawaska, and Canadian Dyno). These facilities are operated by their owners under license from the Canadian Nuclear Safety Commission (CNSC) and are regularly monitored and maintained. The approved safety cases for these facilities and CNSC regulatory oversight are intended to ensure that licensees are protecting the public and the environment. There is no CNSC oversight of the properties where groundwater samples were obtained as part of this study.

All groundwater samples were analyzed for standard chemical and physical parameters. A subset of samples from each field site was analyzed for the radionuclides ^{226}Ra and ^{210}Pb. Groundwater samples were not analyzed for radioactive decay products of ^{232}Th nor were they analyzed for microbiological parameters.

Accompanying Compact Disk

A Compact Disk (CD) accompanying this report contains four data files in Microsoft Excel® format. These files are described as follows:

- of_7992_Bancroft-All.xlsx: file containing entire collated geochemistry data set.
- of_7992_Bancroft-2011.xlsx: file containing geochemical analyses and laboratory QA/QC results for 2011 groundwater samples.
- of_7992_Bancroft-2012.xlsx: file containing geochemical analyses and laboratory QA/QC results for 2012 groundwater samples.
- of_7992_Bancroft-2013.xlsx: file containing geochemical analyses and laboratory QA/QC results for 2013 groundwater samples.

Acknowledgments

This project was supported by the Environmental Geosciences Program of the Earth Sciences Sector of Natural Resources Canada. Judy Vaive and Pierre Pelchat of the Geological Survey of Canada Inorganic Geochemical Research Laboratory performed the water chemistry analyses. Rick McNeil shared unpublished GSC results on uranium concentrations in surface waters in the Bancroft area. Robert Garrett provided helpful comments on a draft version of this report.

STUDY AREA

Climatic and Physiographic Setting

The Bancroft uranium mining district is located in southeastern Ontario, approximately 250 km northeast of Toronto and a similar distance west of Ottawa (Figure 2). It straddles Monmouth and Cardiff Townships of Haliburton County and the western part of Faraday Township in Hastings County. Most of the region is readily accessed by paved or unpaved all-weather roads.

The study area lies within the Algonquin-Lake Nipissing ecoregion of the Boreal Shield ecozone (Wiken, 1986) which extends from Georgian Bay in the west to the Ottawa River Valley in the east (Ecozones, 2014) This ecoregion is classified as having a humid high cool temperate (HCTh) ecoclimate marked by warm summers and cold winters (Strong et al., 1989). At Haliburton (Lat. 45.0322° N; Lon. 78.5311° W; Elev. 330 m), the nearest active weather station, the mean annual temperature is approximately 5.0° C. The mean summer (July) temperature is 18.7° C and the mean winter (January) temperature is -9.9°. Mean annual precipitation is approximately 1074 mm including 794 mm of rainfall and 280 mm of snowfall equivalent (Environment Canada, 2014). Climate data for Haliburton are presented in Table 2.

The study area is underlain by gneissic bedrock forming broad uplands and lowlands. Elevations range from 500 m in the central part of Cardiff Township to 343 m on Paudash Lake. The landscape is strongly glaciated and is characterized by ridged to hummocky rock outcrops covered with discontinuous acidic morainal tills and significant areas of fluvioglacial, and lacustrine deposits. Exposed bedrock is common and soils are generally thin. Humo-Ferric Podzols, associated with dry sites, are the dominant soil type. Gray-brown Luvisols and Melanic Brunisols are found on normally-drained sites (Ecozones, 2014).

Surface drainage patterns are strongly controlled by bedrock lithology and structure. Higher-order radial and concentric drainage networks are developed on the low-permeability igneous domes forming the main uplands. These feed the larger lakes and meandering rivers found in the lowlands associated with more recessive metasediments and metavolcanic rocks that ring the domal structures. The study area is drained by the York River, Crowe River, Irondale River and Eels Creek in the north, east, west and south, respectively. Numerous wetlands include ubiquitous small bogs formed in depressions on the igneous uplands and larger marshes bordering rivers and creeks in the lowlands.

Groundwater flow patterns are controlled by bedrock topography and permeability. The most active groundwater flow systems are developed in the upper bedrock where fractures are pervasive. These shallow systems are recharged in local uplands and discharge to nearby wetlands, creeks and ponds. Deeper groundwater flow systems, controlled by major bedrock structures, extend from regional uplands to large lowland lakes.

Table 2: Climate normals (1981-2010) for Haliburton, Ontario. Data from Environment Canada (2014).

Month	Daily Average (°C)	Daily Maximum (°C)	Daily Minimum (°C)	Rainfall (mm)	Snowfall (cm)	Precipitation (mm)
Jan	-9.9	-3.8	-15.9	33.7	67	100.6
Feb	-9.1	-2.2	-16.0	21.2	53	73.9
Mar	-3.8	3.1	-10.6	37.4	38	75.4
Apr	4.3	10.7	-2.2	56.1	19	75.6
May	11.2	18.2	4.1	90.8	2	93.3
Jun	16.5	23.3	9.7	81.2	0	81.2
Jul	18.7	25.5	11.8	90.1	0	90.1
Aug	17.8	24.5	11.1	79.0	0	79.0
Sep	13.4	19.9	6.9	100.2	0	100.2
Oct	6.8	12.3	1.4	93.1	7	100.2
Nov	0.7	5.2	-3.7	83.4	33	116.4
Dec	-6.4	-1.2	-11.5	27.7	60	87.7
Year	**5.0**	**11.3**	**-1.2**	**794**	**280**	**1073.5**

The dominant vegetation in the ecoregion is mixed-wood forest consisting of sugar maple, yellow birch, eastern hemlock, and eastern white pine, with beech appearing on warmer sites. Dry sites are dominated by red and eastern white pine, and red oak. Wetter sites support red maple, black ash, white spruce, tamarack, and eastern white cedar. Characteristic wildlife includes white-tailed deer, moose, elk, black bear, wolf, lynx, snowshoe hare, squirrel and chipmunk. Bird species include the hooded merganser, American black duck, wood duck, pileated woodpecker, mourning dove, cardinal, and wood thrush (Ecozones, 2014).

Tourism and forestry are the most significant land uses. Low-intensity farming operations are scattered throughout much of the region. Bancroft is the largest population centre. Smaller centres within the study area include Cardiff, Wilberforce and Tory Hill.

Geological Setting

The Grenville Province (Davidson, 1998) is a complex, circa 1100 Ma, orogenic belt that truncates several older geological provinces. In Ontario, it is subdivided from north to south into the Grenville Front Tectonic Zone, the Central Gneiss Belt, and the Central Metasedimentary Belt (Easton, 1992). The Central Metasedimentary Belt Boundary Zone, a band of tectonites several kilometres wide, marks the contact between the Central Gneiss Belt (CGB) and allochtonous terranes of the Central Metasedimentary Belt (CMB) which were thrust over the CGB from the southeast. The CMB constitutes a major Mid-Proterozoic accumulation of supracrustal rocks intruded by compositionally diverse, syntectonic, late tectonic and post-tectonic plutonic rocks, and metamorphosed at grades from greenschist to granulite facies (Easton, 1992). From northwest to southeast, the CMB is subdivided into the Bancroft, Elzevir, Mazinaw, Sharbot Lake and Frontenac lithotectonic terranes (Easton, 1992). The Elzevir Terrane is further divided into the Harvey-Cardiff Arch, Belmont, and Grimsthorpe Domains. The study area is restricted to the northern part of the Harvey-Cardiff Arch and bordering areas of the Bancroft Terrane (Figure 2).

The (1400-1250 Ma) supracrustal rocks of the Bancroft Terrane consist mainly of calcitic and dolomitic marbles with quartz arenite, quartzo-feldspathic gneiss and minor mafic to intermediate metavolcaniclastics. In the Harvey-Cardiff Arch, the (1300-1250 Ma) supracrustal rocks include mafic to felsic metavolcanics, metawackes, metapelites, turbidites, and minor metacarbonates. The Bancroft Shear Zone (Carlson et al., 1990) forms the contact between the shallow-marine carbonates and siliclastics of the Bancroft Terrane and the deeper, active basin volcanics and immature sediments of the Harvey-Cardiff Arch (Easton, 1992).

The supracrustal rocks of the CMB have been intruded by nine major plutonic suites (Easton, 1992), four of which are significant in the study area. The (ca. 1280-1250 Ma) Nepheline Syenite Suite is found almost exclusively within the Bancroft Terrane where it forms several discontinuous belts of small elongated plutons originally emplaced as sills (Lumbers et al., 1990; Easton, 1992). The (1280-1270 Ma) “Elzevir” Tonalite Suite is, by volume, the most abundant plutonic suite within the CMB. It is found in both the Bancroft Terrane and in the Harvey-Cardiff Arch Domain where it is closely associated with metavolcanic rocks (Easton, 1992). Plutonic masses of the Elzevir Suite form the large Glamorgan Gneiss Complex in the Bancroft Terrane and the cores of the Burleigh and Anstruther gneiss domes of the Harvey-Cardiff Arch. The (1250-1240 Ma) “Methuen” Alaskite Suite is the second most abundant plutonic suite within the CMB. In the Bancroft Terrane, this suite occurs as small plutons sometimes intermixed with other plutonic rocks (Lumbers et al., 1990). In the Harvey-Cardiff Arch Domain, alaskite of the Methuen Suite forms the cores of the Cheddar and Cardiff gneiss domes and rims the cores of the older Burleigh and Anstruther tonalite gneiss domes (Easton, 1992). The (1070-1040 Ma) Fenite-Carbonatite and the (1050-1030 Ma) Granite Pegmatite Suites are related post-tectonic, plutonic events associated with uranium mineralization. Fenites, or skarns, characterized by patches and veinlets of alkali pyroxene and amphibole, occur in a band running the length of the Bancroft Terrane paralleling the Central Metasedimentary Belt Boundary Zone (Easton, 1992). The fenitizing fluids introduced sodium, potassium, calcium, iron, titanium, phosphorus, fluorine, chlorine, as well as uranium, thorium, rare earth elements, zirconium, barium and molybdenum into the country rocks (Lumbers et al., 1990).

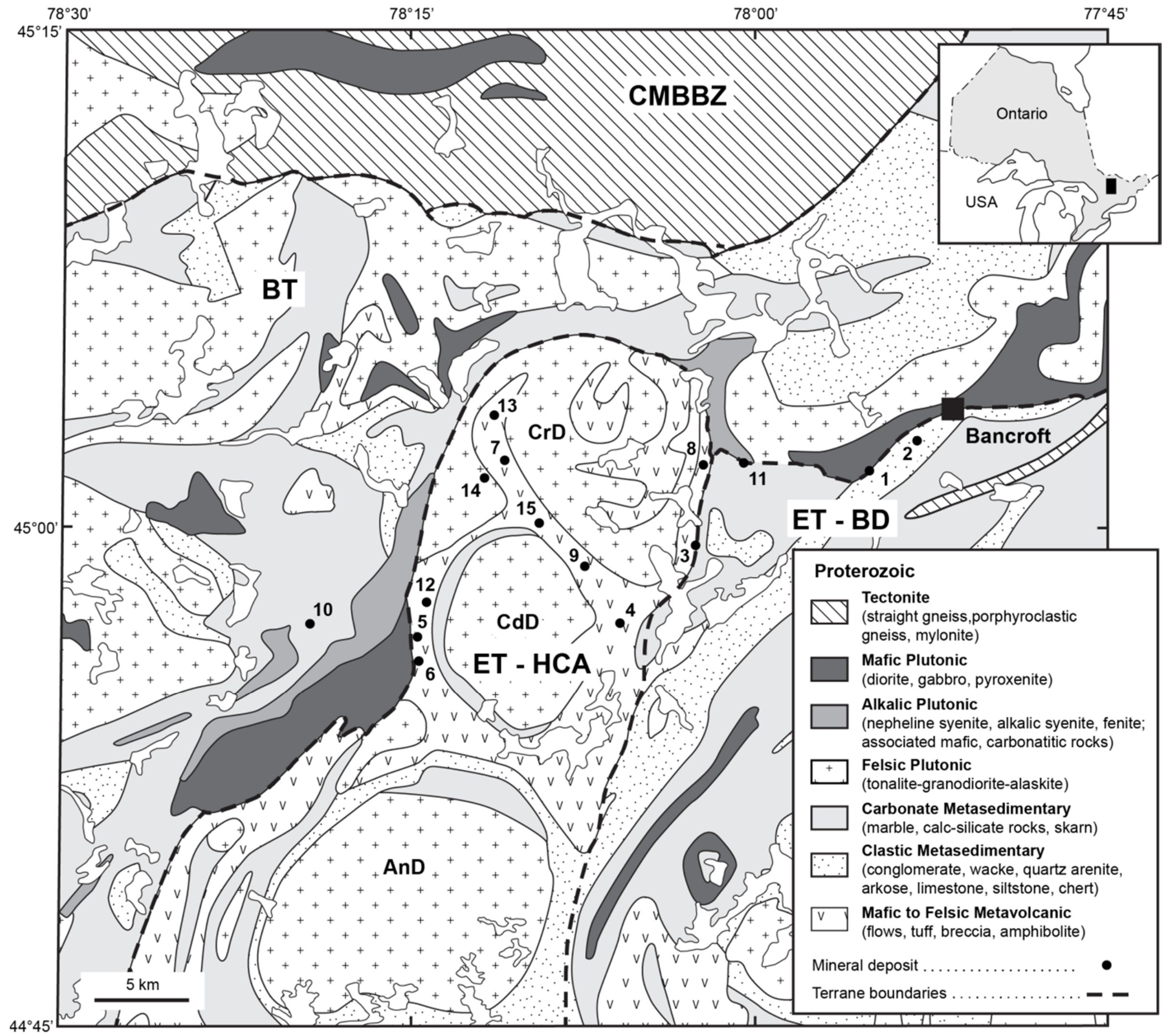

Figure 2: Simplified geological map of the study area showing locations of past producing U mines and selected prospects; (CMBBZ) Central Metasedimentary Belt Boundary Zone; (BT) Bancroft Terrane; (ET-BD) Belmont Domain of the Elzevir Terrane; (ET-HCA) Harvey-Cardiff Arch of the Elzevir Terraine; (AnD) Anstruther Dome; (CdD) Cheddar Dome; (CrD) Cardiff Dome; (1) Madawaska Mine; (2) Greyhawk Mine; (3) Bicroft Mine; (4) Dyno Mine; (5) Amalgamated Rare Earth No.1 Mine; (6) Amalgamated Rare Earth No.2 Mine; (7) Halo Mine; (8) Croft Mine; (9) Canada Radium Mine; (10) Canadian All Metals Mine; (11) Silver Crater Mine; (12) Saranac Prospect; (13) Richardson-Fission Mine; (14) Cardiff Mine; (15) Kenmac-Chibougamau Mine. Map modified from OGS (1991).

Carbonatites follow a similar spatial distribution and occur mainly as narrow, elongated calcite “vein dikes” and, exceptionally, as large irregular calcite bodies. Pegmatites, often uraniferous, occur as long, narrow dikes or sills in the metasediments and metavolcanics that flank the plutonic domes of the Harvey-Cardiff Arch; however, they are also common within the fenite-carbonatite belt in the Bancroft Terrane and along the Bancroft Shear Zone. The spatial distribution of the fenite-carbonatite and pegmatite suites overlaps that of the older nepheline syenites. This suggests that the ca. 1050 Ma alkali metasomatism and the ca. 1290 Ma nepheline syenite plutonism may be structurally controlled by the Central Metasedimentary Belt Boundary Zone (Easton, 1992). The temporal, spatial and geochemical relationship among the granitic pegmatites, skarns and calcite veins hosting uranium, thorium and rare earth mineralization also suggests they share a common magmatic hydrothermal origin (Lumbers et al., 1990; Lentz, 1991; 1996). The locations of mineral deposits in relation to major geological structures and gneiss domes are shown in Figure 3. Their locations in relation to airborne radiometric anomalies are shown in Figure 4.

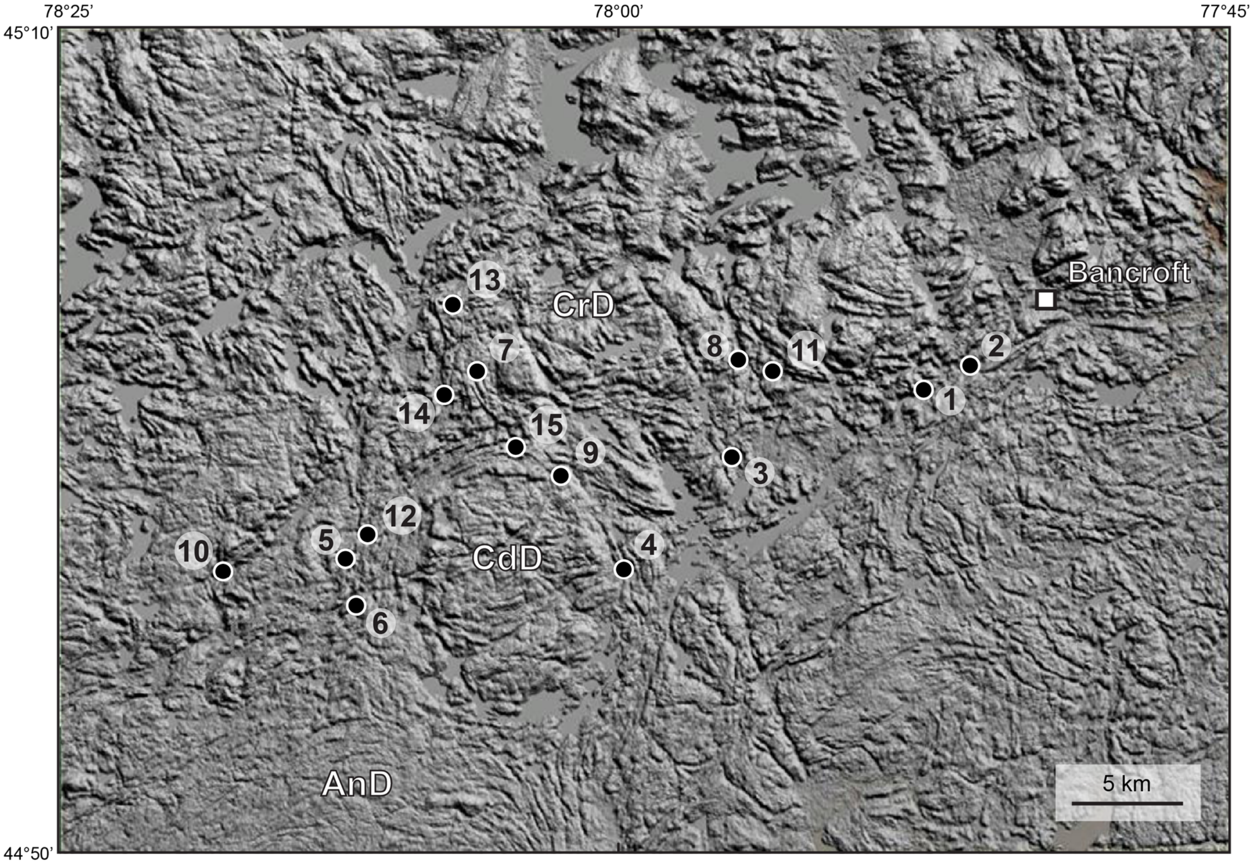

Figure 3: Digital elevation model of the study area showing locations of past producing U mines and selected prospects in relation to geological structure: (AnD) Anstruther Dome; (CdD) Cheddar Dome; (CrD) Cardiff Dome; (1) Madawaska Mine; (2) Greyhawk Mine; (3) Bicroft Mine; (4) Dyno Mine; (5) Amalgamated Rare Earth No.1 Mine; (6) Amalgamated Rare Earth No.2 Mine; (7) Halo Mine; (8) Croft Mine; (9) Canada Radium Mine; (10) Canadian All Metals Mine; (11) Silver Crater Mine; (12) Saranac Prospect; (13) Richardson-Fission Mine; (14) Cardiff Mine; (15) Kenmac-Chibougamau Mine. Map from Ontario (2012).

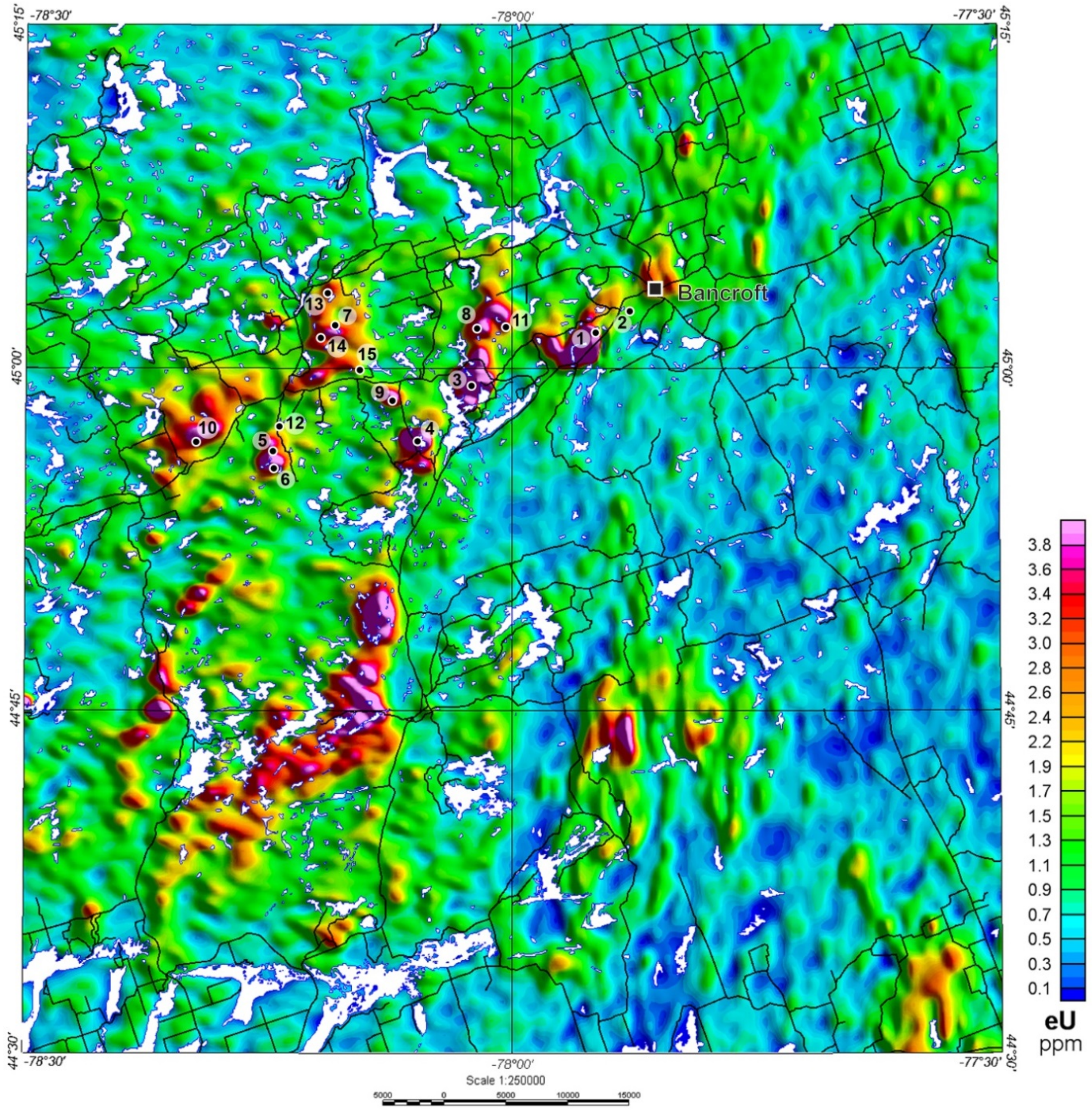

Figure 4: Airborne radiometric map of equivalent U in the study area showing locations of past producing U mines and selected prospects including those sampled as part of this study: (1) Madawaska Mine; (2) Greyhawk Mine; (3) Bicroft Mine; (4) Dyno Mine; (5) Amalgamated Rare Earth #1 Mine; (6) Amalgamated Rare Earth #2 Mine; (7) Halo Mine; (8) Croft Mine; (9) Canada Radium Mine; (10) Canadian All Metals Mine; (11) Silver Crater Mine; (12) Saranac Prospect; (13) Richardson-Fission Mine; (14) Cardiff Mine; (15) Kenmac-Chibougamau Mine. Modified from Carson et al. (2004).

Economic Geology

Satterly (1957) and Lentz (1991) have classified U-Th-REE deposits of the CMB as shown in Table 3. Many deposits of the study area exhibit characteristics of more than one type, such as pegmatite-skarn or pegmatite-vein, as a result of their common genesis.

The mineralogically-simple pegmatites are coarsely crystalline fissure-filling dikes that are usually lenticular, pod-shaped or branching. Some dikes exhibit mineral zonation from wall to core. The pegmatites consist mainly of quartz, microcline perthite, plagioclase and muscovite. They are usually barren or weakly mineralized (Satterly, 1957; Goad, 1990).

Mineralogically-complex pegmatites occur as both intrusive and replacement bodies, with varying degrees of host-rock assimilation. The mineralogical complexity arises from metasomatic hybridization of simple pegmatites with host rocks of varying composition (Lentz, 1996 and references therein). These pegmatites usually contain quartz, microcline perthite, and plagioclase. They may also contain albite, biotite, Ca-pyroxene, hornblende, magnetite, pyrite, calcite, fluorite and accessory minerals bearing uranium, molybdenum and rare earth elements. Uranium, Th and REE mineralization consists primarily of disseminated uraninite and uranothorite with minor to locally-abundant allanite, thorite, thorianite and secondary uranophane. Other accessory minerals include pyrochlore, euxenite, cyrtolite (zircon) and fergusonite (Satterly, 1957; Goad, 1990; Lentz, 1991, 1996; Easton and Fyon, 1992). Mineralization can occur randomly within the pegmatites or in sheared, fractured (cataclastic) parts of the dikes, usually in altered zones near the contacts with host rocks. In larger pegmatites, mineralization occurs in elongated lenticular zones, along and parallel to the contacts, or medial to the dikes. Associated alteration includes silicification, hematization and albitization (Carter, 1984). Higher U grades are typically associated with hematization of feldspars and mafic wall rock xenoliths (Satterly, 1957; Easton and Fyon, 1992). Generally, greater U and REE enrichment of pegmatites is associated with an increased ferromagnesian silicate content caused by host-rock interaction (Lentz, 1996).

Uraniferous skarns form coarse-grained, tabular, lenticular and irregular bodies occurring as marginal zones of granitic pegmatites, as replacement zones and as veins (Lentz, 1991). Marble-hosted skarns are formed as conformable zones along contacts between marbles and paragneiss. Host marbles are calcitic, with minor dolomite, muscovite, quartz, phlogopite, albite, apatite and titanite. Locally, the marbles may be altered to silica-rich assemblages of calcite, diopside, tremolite, phlogopite with sulphides (Satterly, 1957; Lentz, 1991). Uranium mineralization is erratic and consists mainly of disseminated uraninite and uranothorite (Satterly, 1957). Metapyroxenite- or clinopyroxenite-hosted skarns occur as coarse-grained lenticular replacement zones and veins in amphibolite and marble intruded by syenitic or granitic bodies. The clinopyroxenite skarns are composed of pyroxene and mica with accessory apatite, scapolite, titanite, fluorite and uraninite (Satterly, 1957; Lentz, 1991). The distribution of uraninite is erratic but appears to be controlled by the abundance of mica, the presence of scapolite-rich bands, and contacts with pegmatite (Satterly, 1957).

Table 3: Simplified classification of uranium deposits in the Central Metasedimentary Belt of the Grenville Province, after Satterly (1957), Lentz (1991) and Easton and Fyon (1992)

Granite Pegmatites	Simple mineralogy
	Complex mineralogy
Metasomatic Skarns	Marble-hosted
	Metapyroxenite-hosted
Hydrothermal Calcite Veins	Gneiss-hosted
	Amphibolite-hosted
	Marble-hosted
	Metapyroxenite-hosted

Uraniferous hydrothermal calcite veins occur in shear zones and along geological contacts as discontinuous, lenticular fissure-fillings that pinch and swell along strike and dip. In some cases, initial fissure-filling was pegmatite with metasomatic alteration of wall rocks. Later fissure re-opening within the pegmatite was then followed by calcite vein emplacement (Satterly, 1957). In addition to calcite, principal vein minerals include variable amounts of fluorite, apatite and biotite. Accessory diopside, amphibole, biotite, feldspar, titanite and uranium-bearing minerals occur along vein selvages (Lentz, 1991). Generally, selvage composition depends on host-rock composition and may be similar to that of related skarns (Lentz, 1991; Easton and Fyon, 1992). Uranium-bearing minerals consist of uraninite, uranothorite and betafite (Satterly, 1957). The presence of biotite appears to be an important control on the localization of uraniferous mineralization (Satterly, 1957).

Geological Descriptions of Mines and Prospects

Geological descriptions of the main U-Th-REE deposits of the study area are provided in Satterly (1957), Burton, (1984), Griffith (1986) and Alexander (1986). Summary descriptions of all known mineralized occurrences are given by Hewitt (1967), Gordon et al. (1981) and Sabina (1986). The geology of ten mines and prospects visited as part of this study is described here.

Bicroft Mine

The uraniferous pegmatites of the Bicroft mine are hosted within a belt of syenitized and folded metasediments striking N°10 E and dipping 50° E. The zone is overlain by marbles to the east, and is underlain by alaskite of the Cardiff plutonic dome to the west. The metasediments consist of biotite paragneiss, amphibolite, scapolite-biotite gneiss, garnet-sillimanite-biotite paragneiss, and a narrow band of silicated marble. They are intruded by pegmatites which occur as lenticular, en-échelon dikes striking north to northwest and dipping 40-70°E. Mineralized pegmatites are preferentially located within the scapolite and garnet-sillimanite gneiss facies. Ore shoots within the pegmatites are typically located along the foot-wall or hanging-wall contacts and tend to exhibit greater vertical than horizontal continuity. The main pegmatite constituents are quartz, microcline, perthite, peristerite, pyroxene and biotite. Ore minerals are uraninite and uranothorite. Other accessory minerals include allanite, cyrtolite, titanite, fluorite, apatite, calcite, pyrite, pyrrhotite and molybdenite (Gordon et al., 1981; Griffith, 1986).

Croft Mine and Croft South Zone

The Croft deposit and the Croft South Zone lie along strike, in the northern extension of the same metasedimentary belt that hosts the Bicroft deposit. The metasediments consist of amphibolite, hornblende gneiss, biotite paragneiss, and garnet-sillimanite-biotite gneiss. They are cut and replaced by lenticular, en échelon, syenitic and granitic pegmatite dikes. Uranium mineralization occurs within the dikes as shoots emplaced along contacts with garnet-sillimanite-biotite gneiss. Radioactive minerals include uranothorite, uraninite, uranophane, allanite and betafite. Other accessory minerals include tourmaline, cyrtolite, titanite, apatite, graphite, pyrite and molybdenite (Gordon et al., 1981; Burton, 1984; Sabina, 1986).

Amalgamated Rare Earth No.1 Mine

The deposit lies within a band of north-northeast striking amphibolites, quartzites and marbles between the eastern flank of the Glamorgan tonalite gneiss and the western flank of the Cheddar alaskite dome. The host rock is a phlogopite-diopside quartzite containing marble interbeds. Uraniferous pegmatites intrude the quartzite, forming elongated lenses or narrow dikes. The main radioactive minerals are uranothorite and allanite. Other accessory minerals include cyrtolite, pyrite, pyrrhotite and molybdenite (Satterly, 1957; Gordon et al., 1981; Sabina, 1986).

Amalgamated Rare Earth No.2 Mine (formerly Blue Rock Cerium Mine)

The Main Zone of this prospect is hosted by amphibolites and marbles in the same band of metasediments as the Amalgamated Rare Earth No.1 prospect. These rocks are intruded by metagabbro and granitic pegmatite. Uranium mineralization is confined to the pegmatites, which intrude or replace metagabbro, forming small-to-large lenticular bodies. Ore shoots consist of hematized, medium-grained leucogranite with altered pyroxene and abundant cyrtolite and allanite. Radioactive minerals include uranothorite, fergusonite, uraninite and uranophane (Satterly, 1957; Gordon et al., 1981; Sabina, 1986).

Canada Radium Mine

The deposit lies at the contact between alaskite of the Cheddar dome and flanking metasediments striking northwest, parallel to the contact, and dipping steeply to the northeast. The metasediments consist of amphibolite, pyroxene granulite, biotite paragneiss and minor marble beds. They are cut and replaced by numerous small granitic pegmatite dikes emplaced along strike or at right angles. Uranium mineralization occurs in narrow, discontinuous, mafic-rich lenses within the pegmatite. Ore minerals include uraninite and uranothorite. Accessory minerals include uranophane, allanite, calcite, fluorite, apatite, cyrtolite, titanite, magnetite and pyrite (Satterly, 1957; Gordon et al., 1981; Sabina, 1986).

Halo Mine

The deposit is located on the western flank of the Cardiff dome in a curving belt of metasediments striking parallel to the granite contact. The metasediments consist of amphibolite, and biotite or garnet-biotite paragneiss interbedded with marble and metamorphic pyroxenite. In the Northwest Zone of the property, uranium minerals, mainly uraninite, occur in irregular, highly fractured, syenitic or granitic pegmatite lenses characterized by abundant pyroxene and brecciation. Some fractures contain late-stage calcite-pyrite-fluorite veins. Molybdenite, pyrite and pyrrhotite are common accessory sulfides in the pegmatites. In the Lake Zone, U mineralization, mainly uranothorite, occurs within fractured granitic pegmatites containing veins of calcite with abundant accessory pyrite and molybdenite. Higher grade material occurs in quartz-rich pegmatites with accessory cyrtolite, or in hematized cataclastic quartz in pyroxene-rich pegmatites (Satterly, 1957; Gordon et al., 1981; Sabina, 1986).

Canadian All Metals Mine

The deposit is located on the southeastern flank of the Glamorgan tonalite gneiss and is hosted by metasediments striking N 50° E and dipping 30° SE. The metasediments consist of marble, quartzite, paragneiss and granitic gneiss. The mineralization occurs as thorian uraninite and pyrochlore disseminated in discontinuous lenses within zones of silicated marble. The silicated marble contains calcite, tremolite, diopside, phlogopite and serpentine. Other accessory minerals include pyrite and molybdenite (Satterly, 1957; Gordon et al., 1981; Sabina, 1986).

Silver Crater Mine

The deposit lies in a zone situated between a large granitic gneiss complex to the north and marbles and metasediments to the south. The zone consists of syenite, syenitic and nepheline gneiss and biotite-hornblende-plagioclase gneiss. The biotite-hornblende-plagioclase gneiss is intruded by a large sill-like carbonatite body hosting the mineralization. The carbonatite is composed mainly of coarse-grained calcite and black mica. Important accessory minerals include apatite, amphibole and albite. Fluorite, cyrtolite, pyrrhotite and pyrochlore also occur. The main radioactive mineral is betafite (Satterly, 1957; Gordon et al., 1981; Sabina, 1986).

Saranac Prospect

The occurrence lies within a trough of marbles and amphibolites between the eastern flank of the Glamorgan tonalite gneiss and the western flank of the Cheddar alaskite dome. The mineralization is hosted by lenticular bodies of granitic pegmatite intruding hornblende gneiss. Radioactive minerals include uranothorite, uranophane and allanite. Accessory minerals include cyrtolite, titanite and pyrite (Satterly, 1957; Gordon et al., 1981; Sabina, 1986).

METHODOLOGY

Sampling Sites

Hewitt (1967) and Gordon et al. (1981) provide an exhaustive list of U-Th-REE occurrences in Faraday, Cardiff and Monmouth townships west of Bancroft. The objective of field work was to sample groundwater from as many of these occurrences as possible subject to operational and safety considerations. Groundwater from some important occurrences could not be sampled because access to the site was barred by a gate or denied by the property owner. In other cases, recent site restoration activities rendered groundwater inaccessible to sampling. A number of minor occurrences could not be located due to the passage of time since exploration activities occurred. Sampling sites were reached by four-wheel drive vehicle as far as road conditions permitted, and by foot (up to 1 km) for the remainder of the distance. Depending on the extent of mining development at each site, groundwater samples were obtained from flooded shafts, flowing adits, and diamond drill holes (DDH). Shafts and adits were located readily from the directions given in Sabina (1986). Locating historical DDH was more challenging except at the Croft Mine site for which a detailed map was available. Table 4 presents a list of targeted sites along with the sources of groundwater samples, if any.

Groundwater sampling was carried out from September 27 to October 5 in 2011, from September 11 to September 20 in 2012, and from August 21 to August 29 in 2013. Sampling was conducted in late summer or early autumn, near the end of the hydrological year (September 30) when groundwater dilution by recharge from snowmelt is minimal. Over the three field seasons, a total of 41 samples were obtained including 8 duplicates.

Field Procedures

Groundwater samples from shafts and adits were collected using a Waterra Pegasus Athena® 12V peristaltic pump (Figure 5a). Samples from DDH were taken using a Waterra Tornado® 5-stage 12V submersible pump (Figure 5b). Electrical power for the pumps was supplied by Power Sonic® sealed rechargeable 12 Volt (18 Amp-Hour) Absorbed Glass Mat (AGM) deep cycle battery transported by backpack. Groundwater samples from shafts were obtained by passing a 3/8 inch (9.5 mm) LDPE tube through vents installed on the concrete slabs capping the shafts. The peristaltic pump was then used to pump water from the flooded shafts to a flow cell on the surface. Similarly, samples from flowing adits were obtained by pumping water from pools inside the adit portal to a flow cell. Groundwater samples from DDH were obtained using the submersible pump connected to 28 m of 5/8 inch (15.9 mm) LDPE tubing in turn connected to a flow cell. The initial pumping rate averaged approximately 14 L/min but decreased as the water level dropped within the borehole. The maximum pump lift was approximately 26 m (85 ft). For each sampling event, the borehole was purged for 20 minutes and allowed to recover for another 20 minutes. This cycle was repeated two or three times in order to ensure a clear flow prior to sampling from the flow cell. The water level dropped to the pump level within the borehole on only one occasion. Generally, water levels recovered fully between purges. This suggests that host rocks have a relatively high fracture-controlled permeability.

Table 4: Principle mineral deposits and occurrences in the Bancroft area indicating the source(s) and numbers of groundwater samples that were obtained as part of this study.

U-Th-REE Occurrence	Longitude (west)	Latitude (north)	Description	Groundwater sample	Remark
Madawaska-Faraday Mine	77.924	45.021	Former producer (shaft, adit)	-	Access denied by property owner
Greyhawk Mine	77.870	45.031	Former producer (shaft)	-	Access denied by property owner
Canadian Dyno Mine	78.095	44.949	Former producer (shaft)	-	Access denied by property owner
Bicroft Mine	78.033	44.994	Former producer (shaft, adit)	Shaft (1)	Adit backfilled and not flowing
Amalgamated Rare Earth Mine No. 1	78.252	44.953	Advanced prospect (shaft, adit)	Adit (1)	Shaft capped and groundwater inaccessible
Amalgamated Rare Earth Mine No. 2	78.247	44.934	Advanced prospect (shaft, adit, DDH)	Adit (3); DDH (2)	Shaft capped and groundwater inaccessible
Halo Mine	78.178	45.028	Advanced prospect (shaft, 2 adits, DDH)	Adits (2); DDH (2)	
Croft Mine	78.030	45.033	Advanced prospect (adit, DDH)	Adit (3); DDH (15) Stream (1)	
Croft South Zone	78.033	45.006	Prospect (DDH)	DDH (3)	
Canada Radium Mine	78.130	44.986	Advanced prospect (shaft)	Shaft (1)	
Canadian All Metals Mine	78.323	44.947	Advanced prospect (adit, DDH)	DDH (3)	Adit backfilled and not flowing
Silver Crater Mine	78.010	45.029	Advanced prospect (adit, DDH)	Adit (1); DDH (2)	
Saranac East Prospect	78.241	44.962	Prospect (DDH)	DDH (1)	
Richardson-Fission Mine	78.192	45.055	Advanced prospect (adit)	-	Adit backfilled and not flowing
Cardiff Uranium Mine	78.197	45.018	Advanced prospect (shaft, adits)	-	Shaft capped and groundwater inaccessible; adits backfilled
Tripp-Nu-Age Mine	78.178	45.060	Advanced prospect (shaft)	-	Groundwater in shaft inaccessible
Kenmac Chibougamau Mine	78.156	44.997	Advanced prospect (adit, DDH)	-	Adit backfilled and not flowing; DDH dry
Acmac Mine	78.217	45.023	Prospect (adit)	-	Adit dry
Northern Nuclear Mine	78.309	44.921	Prospect (DDH)	-	Gated access

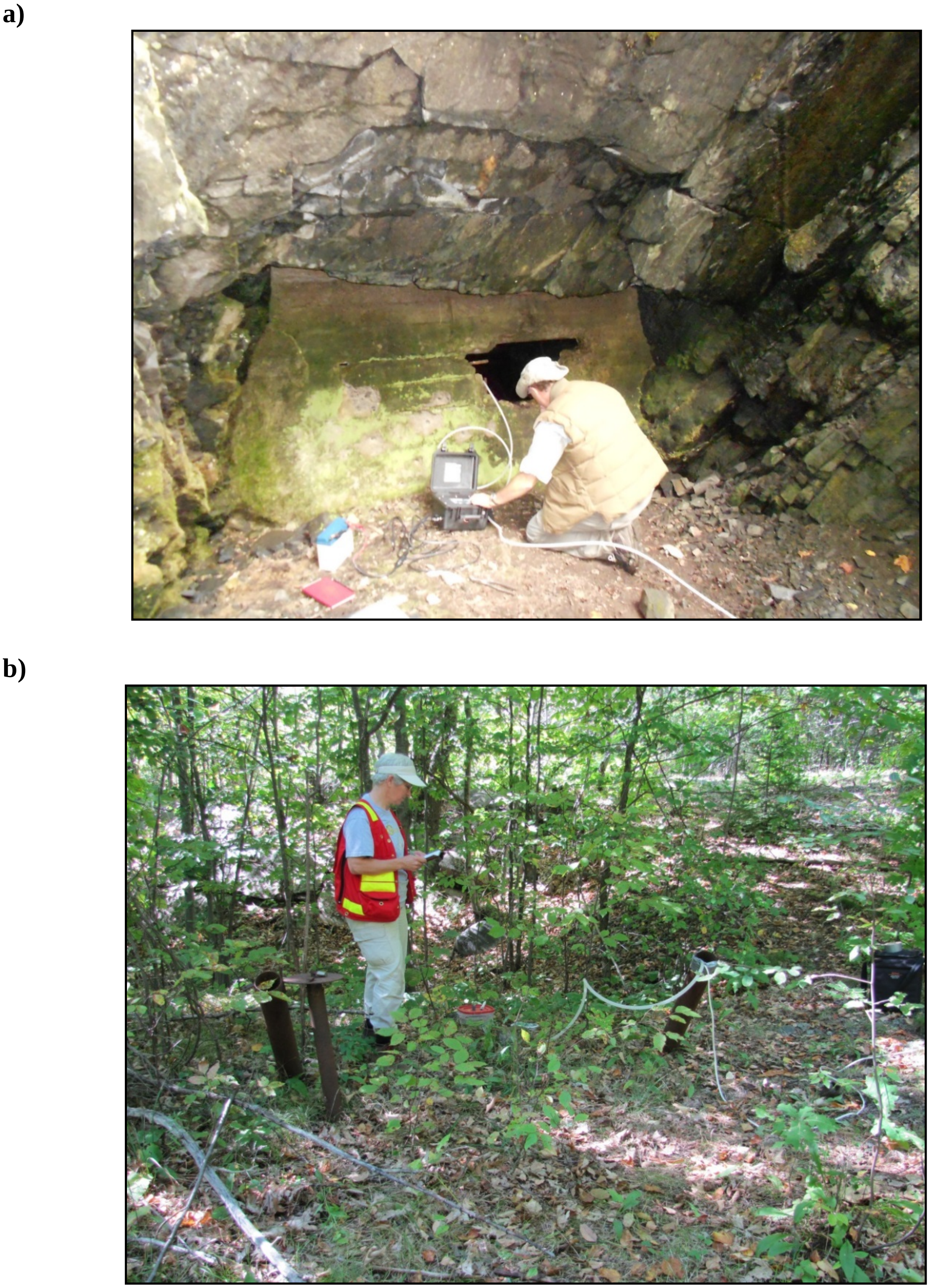

Figure 5: (a) Groundwater sampling from the adit at the Amalgamated Rare Earth No. 2 Mine; **(b)** Sampling from a diamond drill hole at the Croft South Zone.

Flow cells for each pump were constructed out of food-grade plastic containers fitted with a PVC inlet connector to the pump tubing, an outlet spigot, as well as ports for field parameter sensors. Groundwater pH was measured using a Denver Instruments® U-10 meter calibrated daily over the 7-10 range. Specific conductance was measured using an Oakton® CON 11 meter calibrated daily for the 0 to 1413 µS/cm range. Temperature was also measured using the Oakton meter. Field parameters were recorded once values had stabilized in the flow cell.

Groundwater was sampled from the flow cells using all-plastic 50 mL Norm-Ject® syringes triple-rinsed in the water to be sampled. Unfiltered samples for (total) cations were collected in triple-rinsed 60 mL HDPE narrow-mouth bottles (Nalgene® 2002-0002). Filtered (Millipore® Sterivex^{TM} 0.45 µm) samples for anions and cations were collected in 60 mL HDPE narrow-mouth bottles triple-rinsed with filtered water to be sampled. At selected sites, filtered samples for radio-isotopes (^{226}Ra, ^{210}Pb) were collected in triple-rinsed 1 L rectangular HDPE bottles (Nalgene® 2002-0032). Bottles for cation samples were acidified immediately in the field to pH <2 by adding 0.5 mL of 8 N ultrapure nitric acid in pre-measured amounts from 2 mL sterile micro-centrifuge tubes. The 1 L samples for radio-isotopes were acidified at the Inorganic Geochemical Research Laboratory upon return to the Geological Survey of Canada in Ottawa and prior to being sent to a commercial laboratory for analysis.

Duplicate water samples were collected at every tenth sample site, and travel blanks, acid blanks, and sample blanks were prepared once per two-week field program. Samples were stored at 4° C in a hotel room refrigerator pending return to Ottawa.

Laboratory Methods

Groundwater chemistry

All groundwater samples were analyzed at the Inorganic Geochemical Research Laboratory of the Geological Survey of Canada in Ottawa. Analyses of major elements were performed by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) using a Perkin-Elmer 3000 DV. Analyses of trace elements were performed using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) with a Thermo Corporation X-7 Series II. Determinations of anion concentrations were made with a Dionex DX-600 ion chromatograph using an AS-18 column and gradient elution. Alkalinities were determined using a PC-Titrate System. Element suites analyzed by each method and their corresponding detection limits are listed in Table 5. For each sample batch, analyses were performed on one or more certified standards of known concentrations. Analytical results for field blanks from each trip were at or below detection limits for all elements except Cu and Zn. Charge balance errors varied between -6.18% and 4.26% with a mean value of -0.35%.

Radio-isotopes

Filtered and acidified samples for radio-isotope analyses were sent to Becquerel Laboratories Inc. of Mississauga, Ontario. Analyses for ^{226}Ra were performed by alpha spectrometry with a detection limit of 0.01 Bq/L. Analyses for ^{210}Pb were performed by gross beta count (Gas Flow Proportional Counting) with a detection limit of 0.2 Bq/L.

Table 5: Analytical methods and corresponding detection limit for elements analyzed.

ICP-MS Element Suite			
Li (0.02)*	Be (0.005)	B (0.5)	Al (2)
Ti (0.5)	V (0.1)	Cr (0.1)	Mn (0.1)
Co (0.05)	Ni (0.2)	Cu (0.1)	Zn (0.5)
Ga (0.01)	Ge (0.02)	As (0.1)	Se (0.1)
Rb (0.05)	Sr (0.5)	Y (0.01)	Zr (0.05)
Nb (0.01)	Mo (0.05)	Ag (0.005)	Cd (0.02)
In (0.01)	Sn (0.01)	Sb (0.01)	Te (0.02)
Cs (0.01)	Ba (0.2)	La (0.01)	Ce (0.01)
Pr (0.005)	Nd (0.005)	Sm (0.005)	Eu (0.005)
Tb (0.005)	Gd (0.005)	Dy (0.005)	Ho (0.005)
Er (0.005)	Tm (0.005)	Yb (0.005)	Lu (0.005)
Hf (0.01)	Ta (0.01)	W (0.02)	Re (0.005)
Tl (0.005)	Pb (0.01)	Th (0.02)	U (0.005)
* lower detection limit in µg/L shown in brackets			

ICP-AES Element Suite			
Br (0.05)*	Ca (0.02)	Cl (0.1)	Fe (0.005)
K (0.05)	Mg (0.005)	Na (0.05)	P (0.05)
S (0.05)	Sc (0.001)	Si (0.02)	
* lower detection limit in mg/L shown in brackets			

IC Element Suite			
F (0.01)*	Cl (0.01)	SO_4 (0.02)	Br (0.02)
NO_3 (0.02)	PO_4 (0.02)		
* lower detection limit in mg/L shown in brackets			

RESULTS

Field Parameters

The specific conductance (SC) of groundwater is generally higher in more readily weathered host-rocks and with longer residence times or flow paths. Samples obtained from deep DDH are typically associated with long residence times, as are samples from flooded mine shafts. Samples obtained from flowing adits, on the other hand, are associated with relatively short residence times in shallow groundwater systems. Surface area for groundwater-rock interaction is another factor that can influence SC. Thus, greater SC values may be expected in samples from mine workings than from DDH. Specific conductance is plotted here (Figure 6a) against the molar ratio HCO_3/SiO_2 which is used to characterize the relative influence of carbonate versus silicate weathering on groundwater chemistry in the spectrum of U-Th-REE deposits. The highest SC values (> 600 µS/cm) are associated with silicate host-rocks and are observed in samples from deep DDH and from the shaft of the flooded Bicroft mine. Groundwaters associated with marble skarn deposits and carbonatites exhibit intermediate SC values (ca. 400 µS/cm), possibly controlled by calcite dissolution. The lowest values (< 350 µS/cm) are associated with shorter groundwater flow paths in silicate host-rocks.

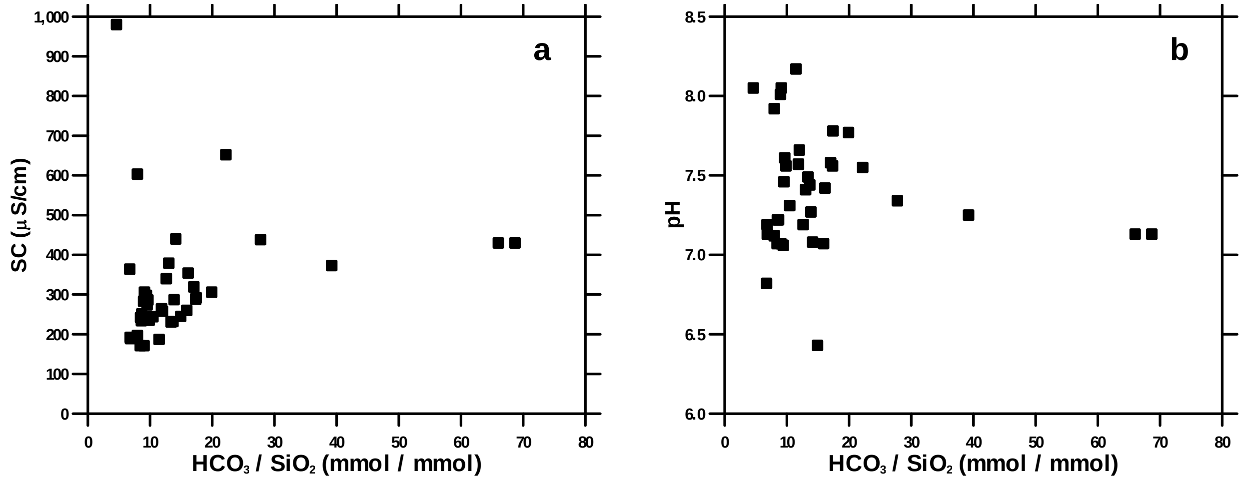

Figure 6: Field parameters: (a) Specific Conductance (SC) versus molar ratio HCO_3/SiO_2; (b) pH versus molar ratio HCO_3/SiO_2. The ratio HCO_3/SiO_2 characterizes the relative influence of carbonate versus silicate host-rock weathering on groundwater chemistry.

The pH of groundwaters reflects geochemical reactions with host-rock minerals. The highest pH values (> 7.5) are associated with the weathering of pyroxenes, amphiboles and feldspars in silicate-hosted deposits (Figure 6b). Values in the range of 7.2-7.5 reflect groundwaters in equilibrium with calcite in marble skarn or carbonatite-hosted deposits. Low values (< 7) are associated with recent recharge from precipitation in shallow bedrock.

Major Dissolved Species

The cation chemistry of groundwaters from Bancroft area U-Th-REE deposits is dominated by Ca (Figure 7). Calcium is derived mainly from calcite weathering in the case of marble skarn or carbonatite deposits. However, calcite is also a common accessory mineral in silicate-hosted U-Th-REE deposits. Additional Ca may be derived from the weathering of amphibole and plagioclase in silicate-hosted deposits. The Mg content of groundwaters is derived from ferromagnesian silicates including amphibole and biotite. The highest Mg fractions are encountered in DDH tapping the metagabbro of the Amalgamated Rare Earth No.2 deposit. The Na and K content of groundwaters reflect weathering of albite and biotite, respectively. Potassium feldspar is not very soluble and is unlikely to contribute much K. The highest fractions of these species are associated with long residence times encountered in deep DDH.

The anion chemistry of groundwaters is dominated by bicarbonate (HCO_3^-) although the sulfate (SO_4^{-2}) content from sulfide (pyrite, pyrrhotite, and molybdenite) oxidation is significant in some samples from deep DDH at the Croft and Halo sites. Anomalous chloride (Cl^-) concentrations are observed in shallow groundwaters sampled in two DDH adjacent to a highway (Croft South Zone). These samples are believed to reflect contamination by road de-icing salt.

Concentrations of dissolved SiO_2 (not shown) cluster close to their mean value of 11 mg/L, possibly reflecting groundwaters that are in equilibrium with a poorly-crystalline silica phase. The highest values are associated with deep DDH and with the flooded Bicroft shaft.

Minor Dissolved Species

Fluoride (F), strontium (Sr), boron (B) and barium (Ba) are other dissolved species of interest (Figure 8). High concentrations of F, B and Ba may pose health risks. Here, however, only two samples slightly exceeded Health Canada (2014) limits for F. No samples exceed limits for B or Ba. Concentrations of minor dissolved species are generally higher in groundwaters associated with granitic pegmatite rather than marble or carbonatite-hosted U-Th-REE mineralization (Figure 9). The highest concentrations reflect extended water-rock interaction as manifested in samples from deep DDH and mine shafts.

While fluorite has been identified in many of the area deposits (Sabina, 1986), dissolved F also may be derived from the weathering of amphibole and mica where it substitutes for the hydroxyl group in the crystal structure (Rimsaite, 1982; Lentz, 1992). In granitic pegmatites, the most likely sources of Sr and Ba are feldspars (K-feldspar, plagioclase) where these elements may replace Ca or K in the crystal structure (Černy et al., 1985). Tourmaline is the most common boron-bearing mineral in the granitic pegmatites of the Bancroft area (Sabina, 1986) although its solubility is low. Concentrations of F and B are well correlated ($r^2 = 0.68$) and this likely reflects the common co-occurrence of fluorite and tourmaline in granitic pegmatite deposits. Generally, the plots in Figure 9 show that the highest concentrations of F, Sr, B and Ba are associated with the weathering of silicate rather than carbonate members of the U-Th-REE deposit spectrum.

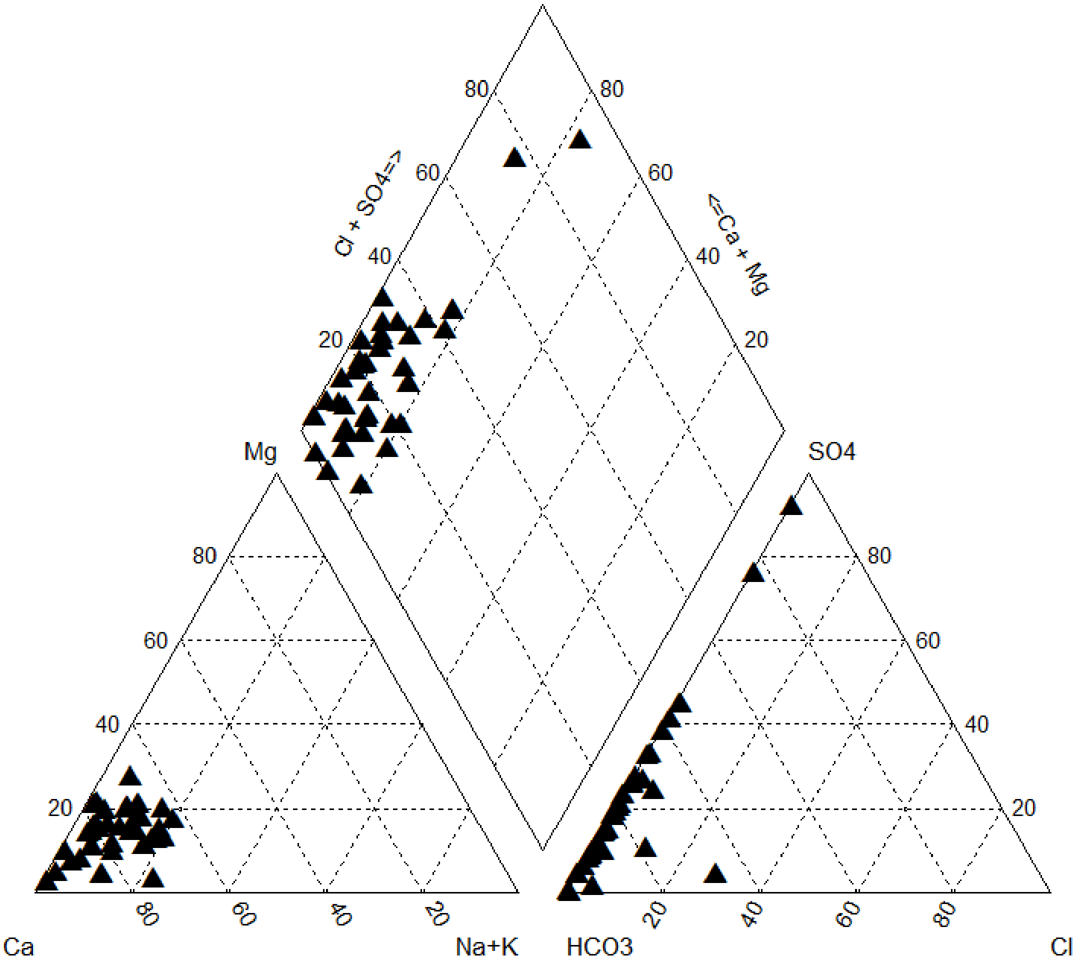

Figure 7: Piper plot of major dissolved species.

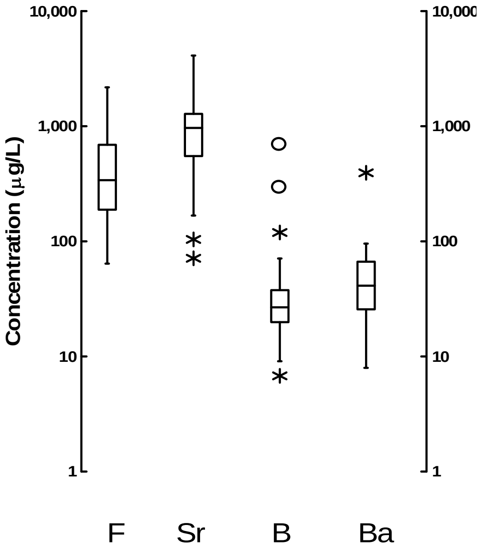

Figure 8: Box-plots of minor dissolved species. Maximum Acceptable Concentrations (MAC) according to Health Canada (2014) are 1.5 mg/L, 5 mg/L, and 1 mg/L for fluoride (F), boron (B), and barium (Ba), respectively. There is no MAC for strontium (Sr). Two samples exceed the MAC for F.

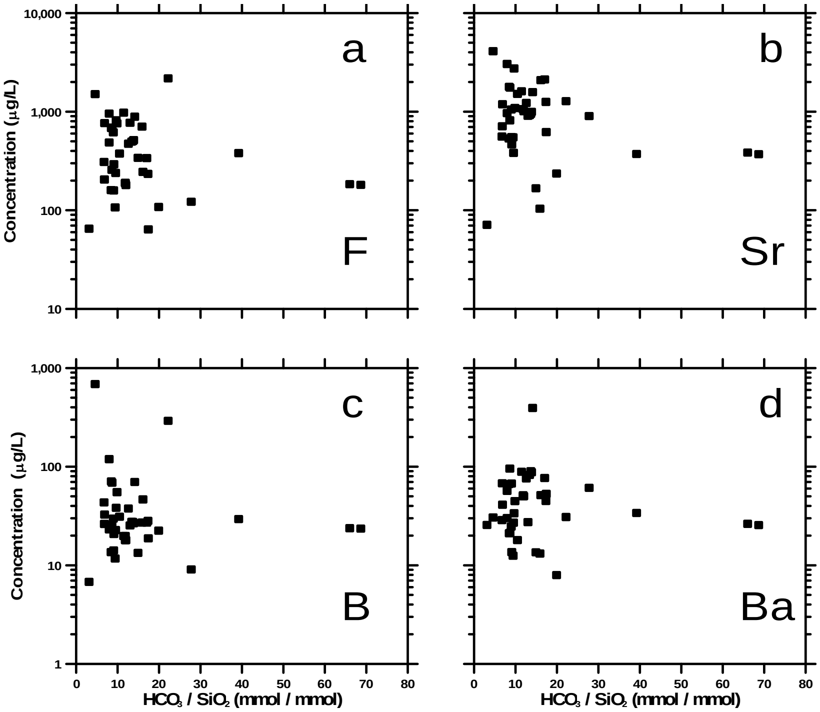

Figure 9: Cross plots of minor species dissolved concentrations versus molar ratio HCO_3/SiO_2: (a) fluoride; (b) strontium; (c) boron; (d) barium. The ratio HCO_3/SiO_2 characterizes the relative influence of carbonate versus silicate host-rock weathering on groundwater chemistry.

Common Metals

Concentrations of the common metals, aluminum (Al), iron (Fe) and manganese (Mn) are of interest because these metals, when in particulate form, have the potential to adsorb trace elements such as U or REE (Figure 10). Generally, total (unfiltered) concentrations of these metals are much higher than dissolved (filtered <0.45 µm) values indicating that most metals occur as suspended particulates including coarse colloids (Figure 10). Here, particulate concentrations are defined operationally as total minus filtered values.

Aluminum in groundwater is derived from the weathering of most silicate minerals. Plagioclase is the most likely principal source. Concentrations of Al in both dissolved and total samples are low. There are no regulatory limits on Al in drinking water because there is no evidence of its toxicity to humans (Health Canada, 2014).

Iron in Bancroft area mine waters is derived mainly from the weathering of ferromagnesian silicate minerals including biotite, pyroxene and amphibole. The oxidation and dissolution of sulfide minerals such as pyrite and pyrrhotite also contributes Fe to groundwaters in some deposits. While there is no evidence of its toxicity to humans, most total Fe concentrations exceed the recommended aesthetic objective of 300 µg/L (Health Canada, 2014). The highest Fe concentrations in the dissolved phase are found in sub-oxic groundwater as in the flooded shaft of the Canada Radium mine.

Manganese in Bancroft area mine waters is derived from the weathering of ferromagnesian silicates where it may substitute for Fe in the mineral structure. Most total Mn concentrations exceed the recommended aesthetic objective of 50 µg/L (Health Canada, 2014). As with Fe, the highest Mn concentrations in the dissolved phase are found in sub-oxic groundwaters.

Trace Elements

The distributions of trace element concentrations in mine waters from U-Th-REE deposits are compared in Figure 11. Corresponding summary statistics are presented in Table 6.

Uranium, in relatively high concentrations, occurs almost entirely in the dissolved phase and is only weakly sorbed on suspended particulates. Thorium, on the other hand, is found in very low dissolved concentrations and is present mostly in the suspended particulate phase. The concentrations of light REE (La-Gd) and heavy REE (Tb-Lu) are also low and REE are mostly sorbed on particulates.

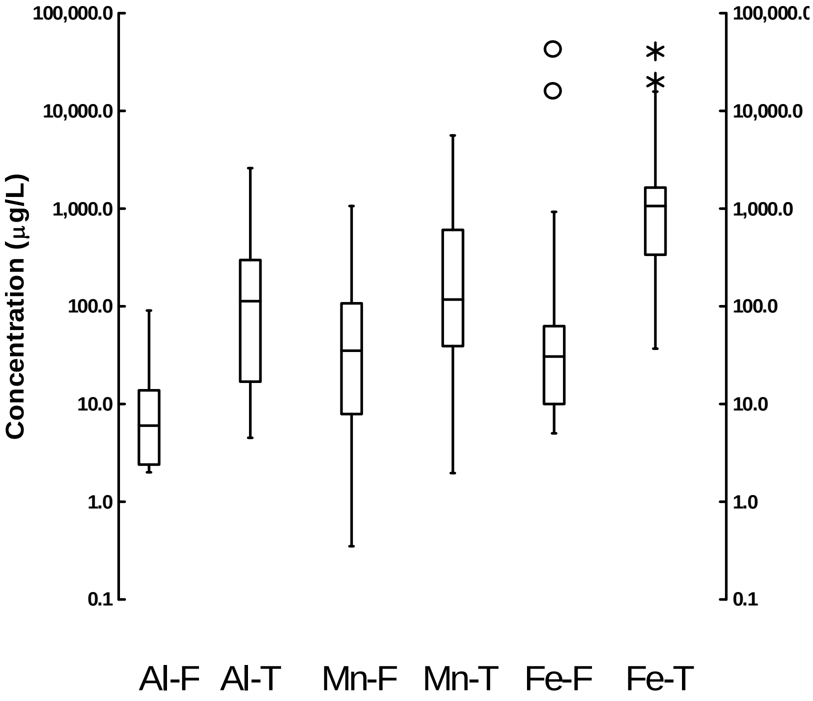

Figure 10: Box-plots displaying the statistical distributions of filtered (F) and total (T) concentrations of the common metals aluminum (Al), manganese (Mn) and iron (Fe).

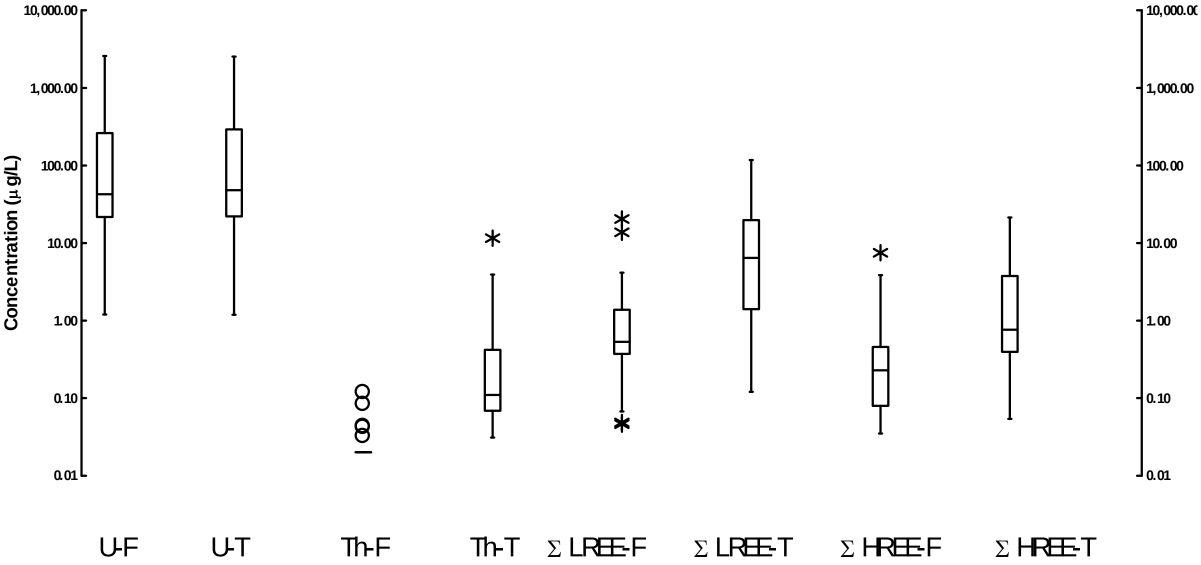

Figure 11: Box-plots displaying the statistical distributions of filtered (F) and total (T) concentrations of the trace elements: uranium (U), thorium (Th), sum of light rare earth elements (Σ LREE), and sum of heavy rare earth elements (Σ HREE).

Table 6: Summary statistics for filtered (F) and total (T) trace element concentrations (in µg/L) in groundwaters from Bancroft area U-Th-REE deposits. Note that analyses of Th were unavailable for 2011 samples.

	U-F	U-T	Th-F	Th-T	Σ LREE-F	Σ LREE-T	Σ HREE-F	Σ HREE-T
n	40	40	27	27	40	40	40	40
Minimum	1.2	1.2	0.02	0.03	0.05	0.12	0.03	0.05
Maximum	2579.7	2530.4	0.12	11.56	20.36	117.43	7.50	21.33
Median	42.6	48.1	0.02	0.11	0.53	6.42	0.23	0.76
Interquartile Range	240.5	269.6	0.00	0.36	1.01	18.34	0.38	3.37
Mean	203.37	213.88	0.03	0.80	2.12	7.00	2.35	16.82
Standard Deviation	434.4	428.3	0.02	2.29	3.75	23.33	1.35	3.97

Relationships between trace element concentrations in groundwater and dominant ore deposit host-rock composition (Figure 12) indicate that the highest uranium concentrations (U > 100 µg/L) are associated with silicate host-rocks (granitic pegmatites) where the main U-bearing minerals are uraninite and uranothorite (Satterly, 1957). Intermediate concentrations (20 < U < 100 µg/L) are associated with a skarn-type deposit (Canadian All Metals) and a carbonatite dike (Silver Crater). At the skarn deposit, the main U-bearing minerals are thorian uraninite and thorianite (Sabina, 1986). The main U-bearing minerals at the carbonatite-hosted deposit are betafite and euxenite (Sabina, 1986). The highest thorium concentrations are also associated with granitic pegmatite deposits where Th is found in uranothorite and thorian uraninite (Satterly, 1957). Thorium concentrations are very low in the carbonatite deposit where Th may be a trace constituent of euxenite. Light REE (La-Gd) concentrations are highest in granitic pegmatite deposits where allanite (Peterson and MacFarlane, 1993) is the main LREE-bearing mineral. Intermediate levels of LREE are observed in the carbonatite deposit where euxenite is the most likely source. Heavy REE (Tb-Lu) concentrations are highest in both granitic pegmatite and carbonatite end-members of the U-Th-REE deposit spectrum. The source of HREE in granitic pegmatites is unclear and may involve a number of minerals. In the carbonatite, the sources of HREE are most likely betafite and euxenite.

Ore deposit type and host mineralogy are important factors controlling the concentrations of trace elements in mine waters. Other key factors are reviewed in the following sections as they apply to each trace element.

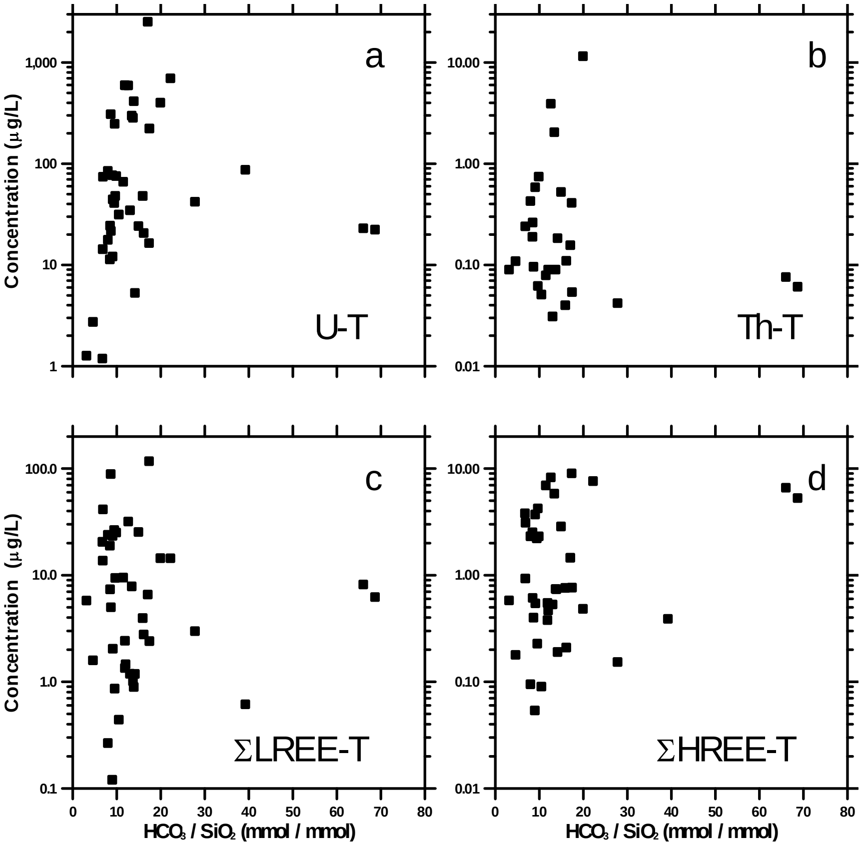

Figure 12: Cross plots of total trace element concentrations versus molar ratio HCO_3/SiO_2: (a) uranium; (b) thorium (c) sum light REE (La-Gd); (d) sum heavy REE (Tb-Lu). The ratio HCO_3/SiO_2 characterizes the relative influence of carbonate versus silicate host-rock weathering on groundwater chemistry.

Uranium and its radioactive decay products

Under reducing conditions, the solubility of uraninite and uranothorite is extremely low and U is almost immobile. Using dissolved Fe concentration as a proxy for redox potential, Figure 13a shows the low U concentrations associated with reducing conditions (high dissolved Fe). However, under more oxidizing conditions, the dissolution of uraninite and uranothorite is greatly enhanced through the formation of stable uranyl (UO_2^{2+}) complexes with carbonate or phosphate ions (Langmuir, 1978) and ternary complexing species such as calcium and magnesium (Bernhard et al., 1996; Kelly et al., 2007). Although apatite is an accessory mineral in some deposits, phosphate concentrations are negligible and uranyl-carbonate or uranyl-Ca-carbonate complexes are responsible for U mobilization (Desbarats et al., 2016). The increased U mobility due to carbonate complexation is illustrated in Figure 13b which shows the general increase in U with alkalinity. Departures from this trend are associated with skarns or carbonatites and reflect the lower U grades in these deposits. Generally, the highest U concentrations are observed under oxic conditions when abundant dissolved Ca and carbonate species are available for complexation. Uranium adsorption is limited except when particulate Fe concentrations are high (Figure 14).

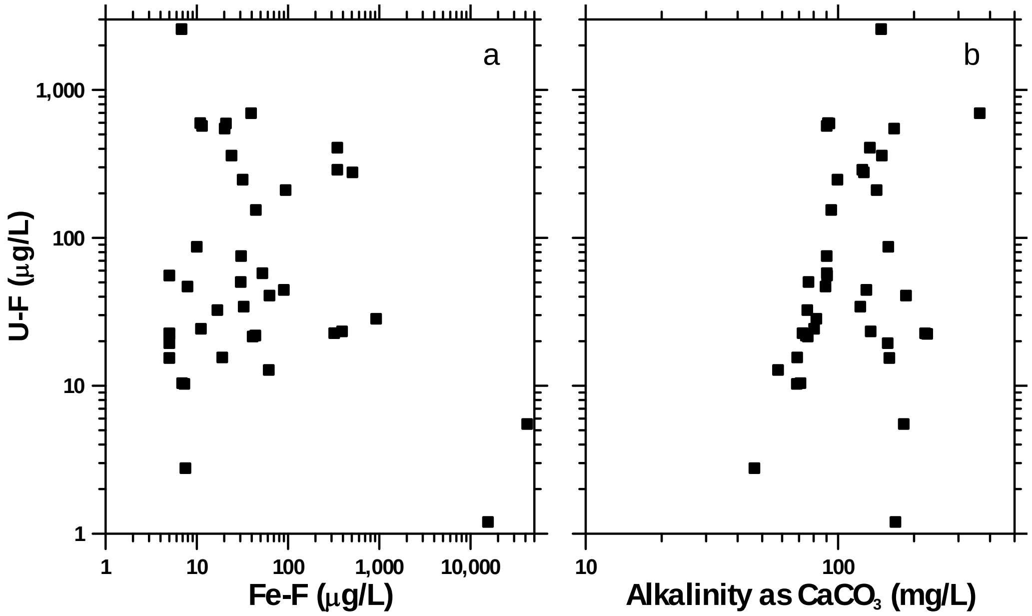

Figure 13: Controls on uranium mobility in groundwater: (a) U versus dissolved (filtered) Fe, a proxy for redox potential; (b) U versus alkalinity, a proxy for carbonate complexing agents.

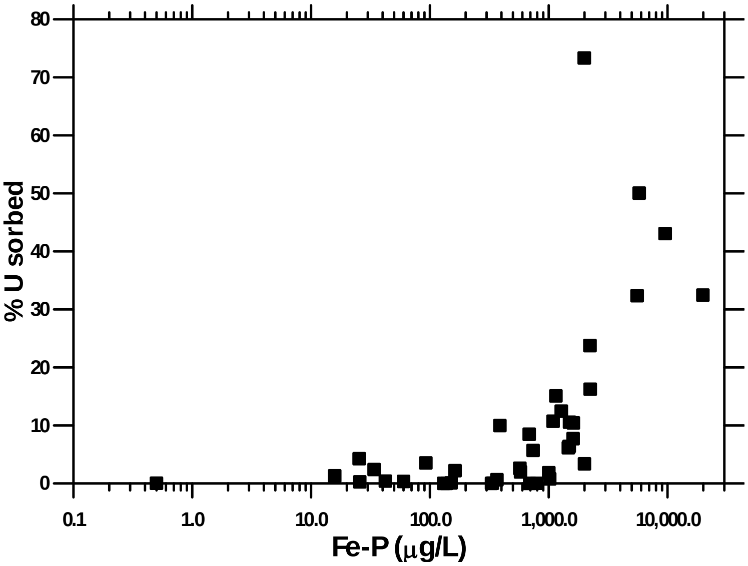

Figure 14: Controls on uranium mobility in groundwater: Adsorption on suspended particulate Fe oxyhydroxides

In groundwater, natural U occurs mainly as ^{238}U and as ^{234}U from its decay series, with half lives of 4468 x 10^6 and 247 x 10^3 years, respectively. Radioactive decay of ^{238}U creates other daughter products including ^{226}Ra and ^{210}Pb with half-lives of 1620 and 21 years, respectively. The relationships between these radionuclides and U (Figure 15) show that groundwaters exhibiting U concentrations less than the Maximum Acceptable Concentration of 20 µg/L (Health Canada, 2014) are unlikely to exhibit Ra and Pb radionuclide activities in excess of regulatory limits.

As observed by others (Asikainen, 1981; Gascoyne, 1989; Szabo and Zapecza, 1991), there is no strong correlation between the concentration of U and the activity of ^{226}Ra (Figure 15a). This is because of the different mobilities of these species in the groundwater environment and because U and ^{226}Ra are separated in the ^{238}U decay series by the long-lived and almost insoluble isotope ^{230}Th (Gascoyne, 1989; Wanty and Schoen, 1991). The plot of U versus ^{210}Pb (Figure 15b) does not suggest any simple correlation between these species either. However, a plot of ^{210}Pb versus ^{226}Ra (not shown) reveals a moderate correlation ($r^2 = 0.68$; n=17) between the activities of these decay products. This suggests a greater degree of equilibrium between radionuclides separated by relatively short-lived isotopes in the ^{238}U decay chain.

Thorium

In Bancroft area deposits, uranothorite is the principal mineral in which Th occurs as a major constituent. However, Th is also a minor constituent in local uraninites and in several exotic minerals including cyrtolite, euxenite and monazite (Sabina, 1986). The thorium content of Bancroft uraninites and uranothorites is described by Robinson and Sabina (1955) and Robinson and Abbey (1957), and in Satterly (1957).

Most thorium-bearing minerals are quite refractory to weathering and Th is considered essentially immobile in most natural waters (Wanty and Schoen, 1991). Here, however, Th is released along with U from more readily dissolved uraninite and uranothorite. Based on the stoichiometry of these minerals, Th concentrations in groundwater should be much higher than those shown in Figure 11. Mass balance considerations suggest that most Th must be immobilized very close to its source. Most of the remainder occurs in the suspended particulate phase. Suspended particulate concentrations of Th are correlated with particulate concentrations of Al, Fe and Mn (Figure 16) suggesting that Th may be sorbed to oxyhydroxides of each of these metals. However, this may be a statistical artefact caused by weak cross-correlations among Al, Fe and Mn particulate concentrations: A Th correlation with any one of these metals would yield an apparent correlation with the others. Here, based on the lesser degree of data scatter in Figure 16b, sorption of Th on Fe oxyhydroxides appears most likely.

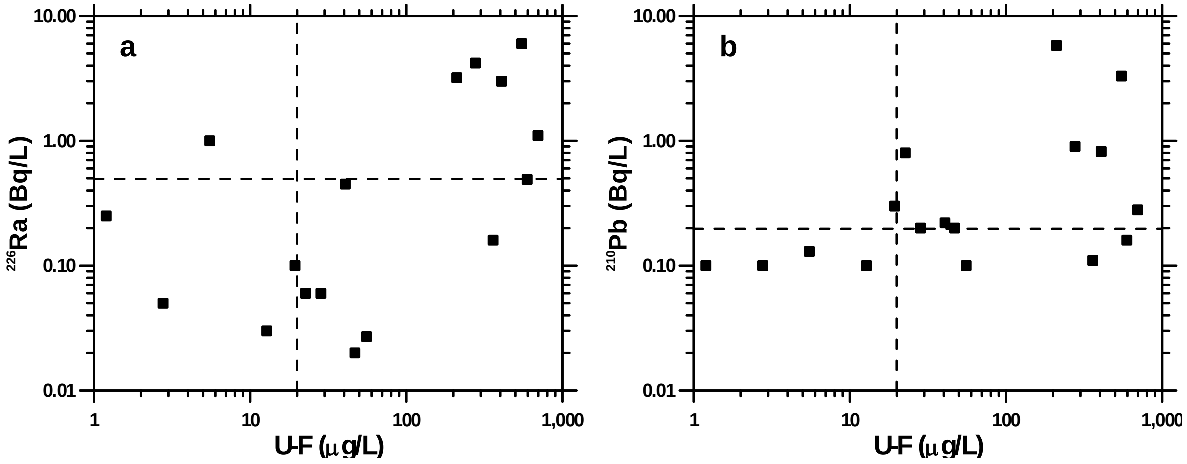

Figure 15: Relationship between U concentration (filtered) and concentrations (filtered) of radionuclide daughter products: (a) Ra-226; (b) Pb-210. Dashed lines represent Health Canada (2014) maximum acceptable concentrations or activities for U (20 µg/L), Ra-226 (0.5 Bq/L) and Pb-210 (0.2 Bq/L).

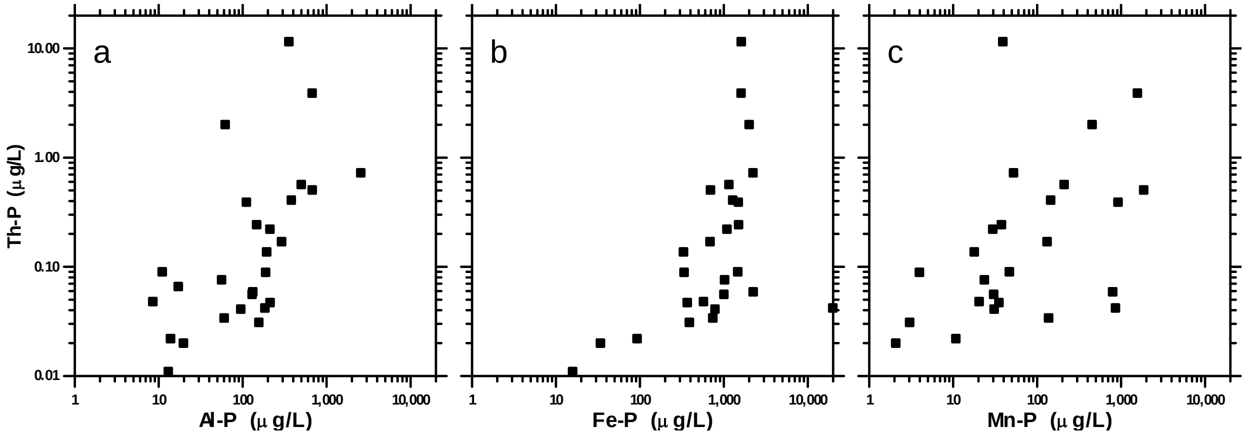

Figure 16: Adsorption of suspended particulate Th on possible sorbents: (a) particulate Al; (b) particulate Fe; (c) particulate Mn.

Rare Earth Elements

In Bancroft area granitic pegmatite deposits, allanite (Peterson and MacFarlane, 1993) is the main source of LREE in groundwater whereas the source of HREE is unknown and may involve a number of minerals (Goad, 1990). In carbonatite deposits, betafite and euxenite may be the sources of both LREE and HREE. As shown in Figure 11, REE in groundwater occur primarily in the suspended particulate phase, adsorbed on oxyhydroxide precipitates of common metals. Sorption of representative LREE (La) and HREE (Dy) on Al, Fe and Mn particulates is investigated in Figure 17. This figure shows varying degrees of correlation between particulate REE and sorbent concentrations. However, based on correlation strength, both LREE and HREE appear to sorb preferentially on Mn oxyhydroxide particulates.

The analysis of REE concentrations can be a powerful tool for understanding geochemical processes (Smedley, 1991; Johannesson, 2004). The utility of REE is derived from their unique and chemically coherent properties: all 14 naturally occurring REE share a trivalent charge and similar ionic radii that decrease systematically with increasing atomic number across the Lanthanide series. Geochemical processes affected by valence fractionate REE from their divalent and tetravalent neighbours in the Periodic Table. They may also fractionate Ce and Eu from other REE because these elements also occur in tetravalent and divalent states, respectively. Geochemical processes affected by ionic radius fractionate REE within the series according to atomic number. Therefore, in the present context, REE concentrations in groundwater reflect original abundances in host rocks as well as the combined fractionation processes associated with REE mobilization. These processes include dissolution of REE-bearing minerals, aqueous complexation, and adsorption.

In the analysis of REE data, it is customary to normalize measured concentrations by corresponding REE abundances in a standard reference material. Here, REE concentrations are normalized with respect to the C1-Chondrite abundances of Anders and Grevesse (1989). REE fractionation patterns are characterized using “profile-plots” showing normalized concentration versus REE in order of increasing atomic number.

Fractionation patterns of REE in mineralized granitic pegmatite host rocks from deposits in the study area have been investigated by Lentz (1996) and are shown in Figure 18. While total REE relative abundances are variable, two types of patterns may be recognized. Patterns of the first type are represented by samples from the Saranac, Amalgamated Rare Earth No.1 and Bicroft deposits. These patterns are characterized by relative enrichment in LREE and generally decreasing relative abundances with atomic number. The LREE enrichment is likely due to the notable occurrence of allanite in these deposits (Gordon et al., 1981). The second type of pattern is represented by the sample from the Halo deposit. This type of pattern is characterized by a slightly concave profile and it is likely that REE occur in a number of minerals including betafite and cyrtolite (Sabina, 1986).

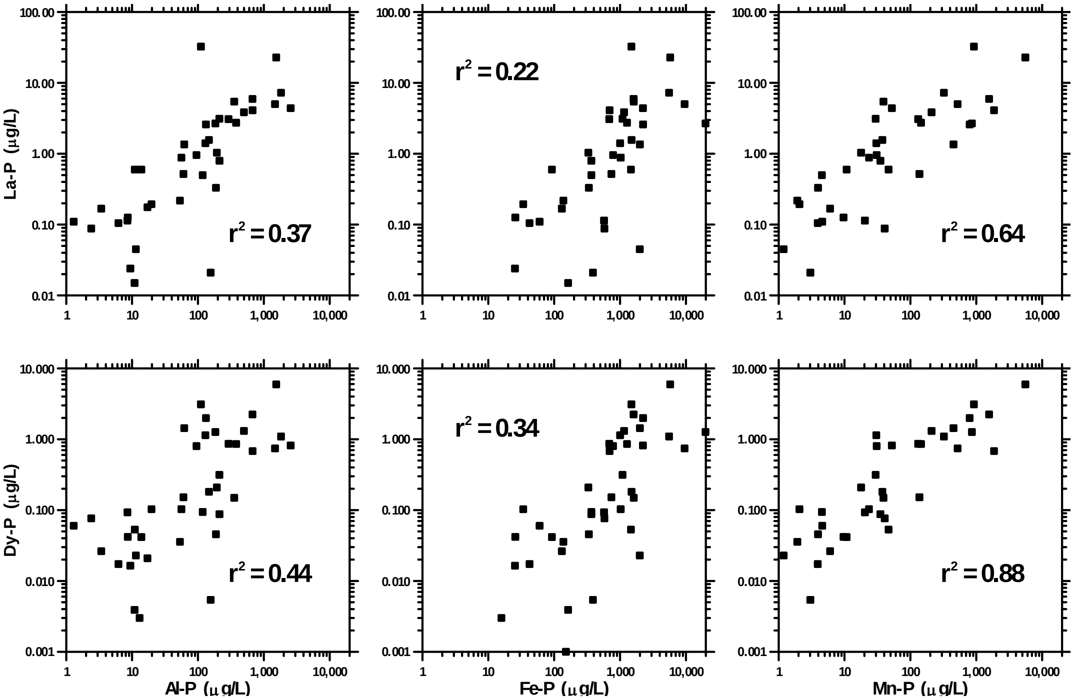

Figure 17: Sorption of representative LREE (La) and HREE (Dy) on potential sorptive metal oxyhydroxides: (top) concentrations of particulate La versus particulate Al, Fe and Mn; (bottom) concentrations of particulate Dy versus particulate Al, Fe and Mn.

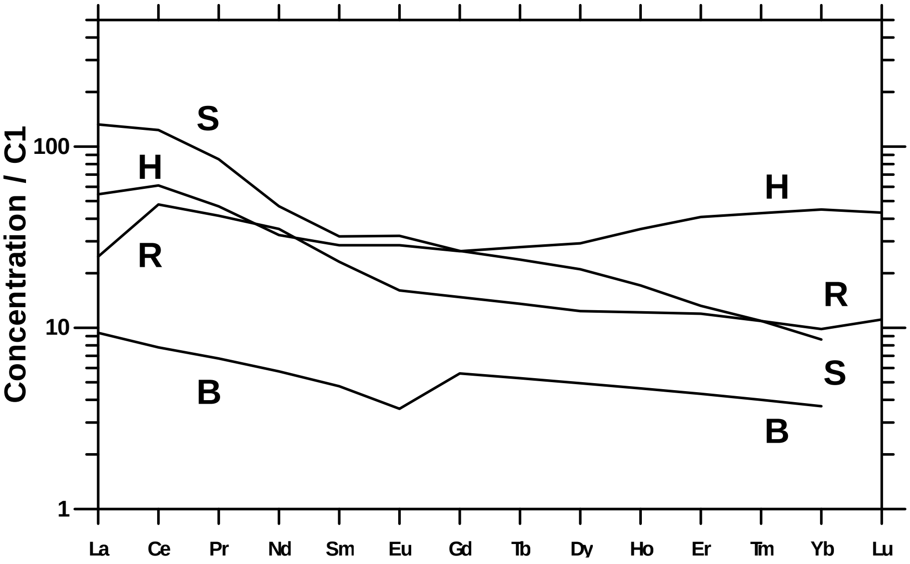

Figure 18: Chondrite-normalized REE patterns for whole-rock samples from selected granitic pegmatite U-Th-REE deposits: (B) Bicroft; (H) Halo; (R) Rare Earth No. 1; (S) Saranac. The whole-rock chemistry data are from Table 1 of Lentz (1996). C1-chondrite abundances are from Anders and Grevesse (1989).

Fractionation processes, such as preferential dissolution of certain REE-bearing minerals, complexation and adsorption, act upon the REE composition of mineralized host rocks yielding transformed REE distribution patterns in groundwater. Distribution patterns for each of the deposits investigated in this study are displayed below (Figures 19-28). These figures show REE patterns for both the dissolved (filtered) and suspended particulate groundwater phases. Total relative REE abundances in groundwater are approximately three orders of magnitude lower than in the granitic pegmatite host rocks of Figure 18.

At the Croft deposit, REE fractionation patterns in the dissolved phase (Figure 19a) are generally flat, indicating no preferential enrichment or depletion according to atomic number. A few samples, however, exhibit significant negative anomalies in Ce abundance. This type of anomaly is observed in more oxic groundwaters where Ce as Ce(IV) is removed by oxidative precipitation of insoluble CeO_2. Fractionation patterns in the suspended particulate phase (Figure 19b) indicate a slight enrichment in LREE due to their preferential sorption on Mn oxyhydroxides (Desbarats et al., 2016). Most profiles also exhibit small negative anomalies in Eu abundance. These anomalies are caused by the preferential incorporation of Eu as Eu(II) into the atomic structure of plagioclase at the time of mineral crystallization. Thus, negative Eu anomalies are generally associated with plagioclase-poor host rock compositions. Figure 19 also shows that relative REE abundances in the particulate phase are typically orders of magnitude higher than in the dissolved phase.

At the Croft South Zone deposit (Figure 20), groundwaters from DDH show REE fractionation patterns in both the dissolved and particulate phases with a slight enrichment in LREE and moderate negative Eu anomalies.

At the Bicroft mine (Figure 21), the REE fractionation pattern in groundwater from the flooded shaft suggests a slight depletion of middle-range REE (Nd-Ho), or MREE, and a moderate negative Eu anomaly. Similar patterns are observed in both the dissolved and particulate phases although relative REE concentrations in the dissolved phase are significantly higher.

At the Amalgamated Rare Earth No.2 deposit (Figure 22), REE fractionation patterns in both the dissolved and particulate phases indicate a slight depletion of MREE (Nd-Ho) and moderate Eu anomalies. These patterns are similar to those observed at the Bicroft mine.

At the Halo deposit (Figure 23), the REE fractionation patterns in the dissolved phases are generally flat although small Ce or Eu anomalies are observed in some samples. Fractionation patterns in the particulate phase suggest a slight enrichment in LREE.

In groundwater from the flooded shaft of the Canada Radium mine (Figure 24), the REE fractionation pattern in the dissolved phase shows a slight depletion in MREE (or enrichment in LREE and HREE). A positive Eu anomaly is also observed. The fractionation pattern in the particulate phase indicates a slight LREE enrichment.

At the Saranac deposit (Figure 25), groundwater from a DDH exhibits a slightly concave fractionation pattern in the dissolved phase suggesting depletion of MREE or enrichment of LREE and HREE. A similar pattern is observed in the particulate phase albeit with a pronounced negative Eu anomaly.

At the Amalgamated Rare Earth No.1 deposit (Figure 26), adit drainage exhibits an essentially flat REE fractionation pattern in the dissolved phase. The saw tooth profile is an artefact of the very low relative abundances. The fractionation pattern in the particulate phase shows enrichment in LREE and a small negative Eu anomaly.

At the Canadian All Metals deposit (Figure 27), groundwaters from DDH exhibit fractionation patterns in the dissolved phase that are slightly enriched in LREE. Two samples show pronounced negative Ce anomalies. Fractionation patterns in the particulate phase are characterized by enrichment in LREE. One sample shows elevated relative REE abundances.

At the Silver Crater deposit (Figure 28), the fractionation pattern in the dissolved phase suggests enrichment in HREE. Duplicate samples from a shallow DDH exhibit pronounced negative Ce and Eu anomalies whereas the sample from the adit does not. The fractionation pattern in the particulate phase is flat albeit with negative Ce and Eu anomalies.

Based on the figures above, REE fractionation patterns can be grouped according to ore deposit type. In groundwaters associated with granitic pegmatite U-Th-REE deposits (Bicroft, Croft, Croft South Zone, Halo, Canada Radium, Amalgamated Rare Earth No.1, Amalgamated Rare Earth No.2, Saranac), REE fractionation patterns in the dissolved phase are slightly concave whereas patterns in the particulate phase show enrichment in LREE. Negative Eu anomalies may be observed in both dissolved and particulate fractionation patterns. It is apparent from these results that REE patterns observed on host-rock samples from granitic pegmatite deposits (Figure 18) are not simply transferred to REE concentrations in groundwater contrary to the findings of Smedley (1991). In groundwaters associated with skarn-type deposits (Canadian All Metals), REE fractionation patterns in both the dissolved and particulate phases' exhibit enrichment in LREE. In groundwaters associated with carbonatite-type deposits (Silver Crater), REE fractionation patterns in the dissolved phase suggest enrichment in HREE whereas patterns in the particulate phase are essentially flat, albeit with prominent Eu anomalies. Negative Ce anomalies are observed in fractionation patterns from all three deposit types and are related to local groundwater redox conditions rather than host rock composition (Desbarats et al., 2016).

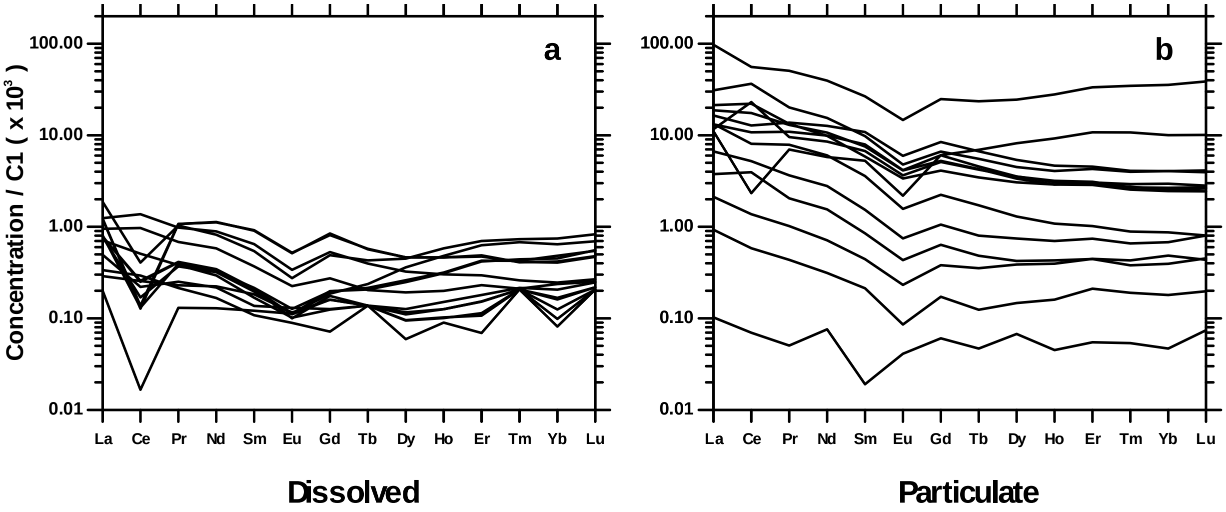

Figure 19: Chondrite-normalized REE patterns for groundwaters from the Croft deposit: (a) dissolved concentrations; (b) suspended particulate concentrations. C1-chondrite abundances are from Anders and Grevesse (1989).

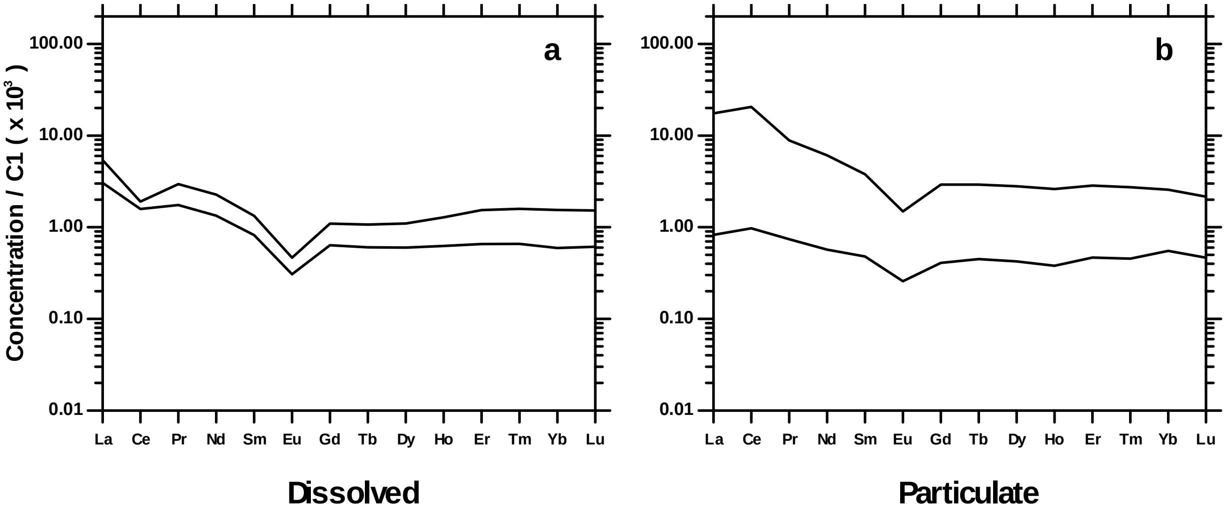

Figure 20: Chondrite-normalized REE patterns for groundwaters from the Croft South Zone deposit: (a) dissolved concentrations; (b) suspended particulate concentrations. C1-chondrite abundances are from Anders and Grevesse (1989).

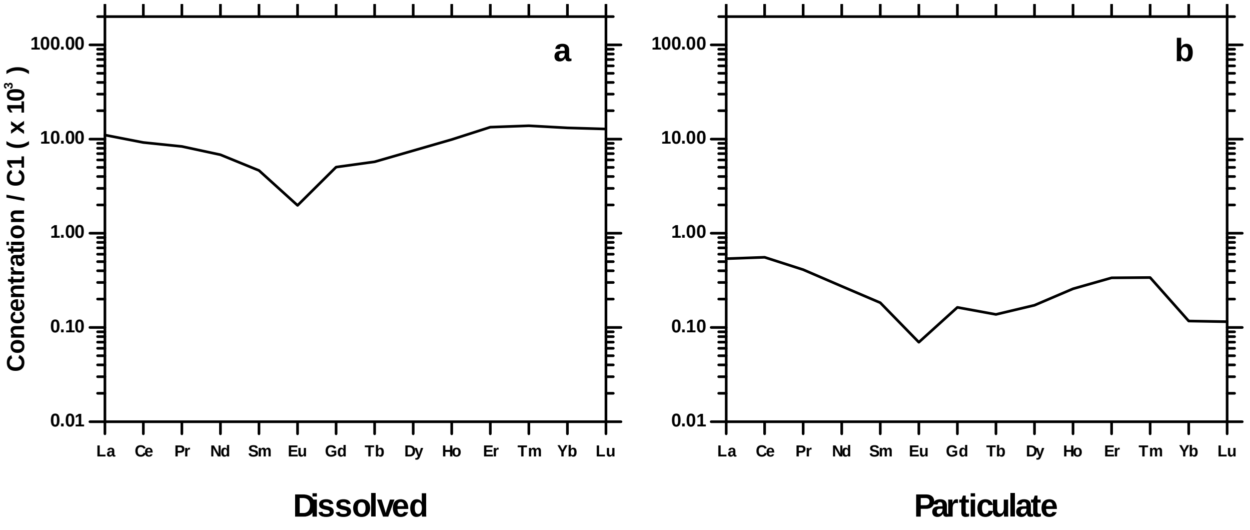

Figure 21: Chondrite-normalized REE patterns for groundwater from the Bicroft deposit: (a) dissolved concentrations; (b) suspended particulate concentrations. C1-chondrite abundances are from Anders and Grevesse (1989).

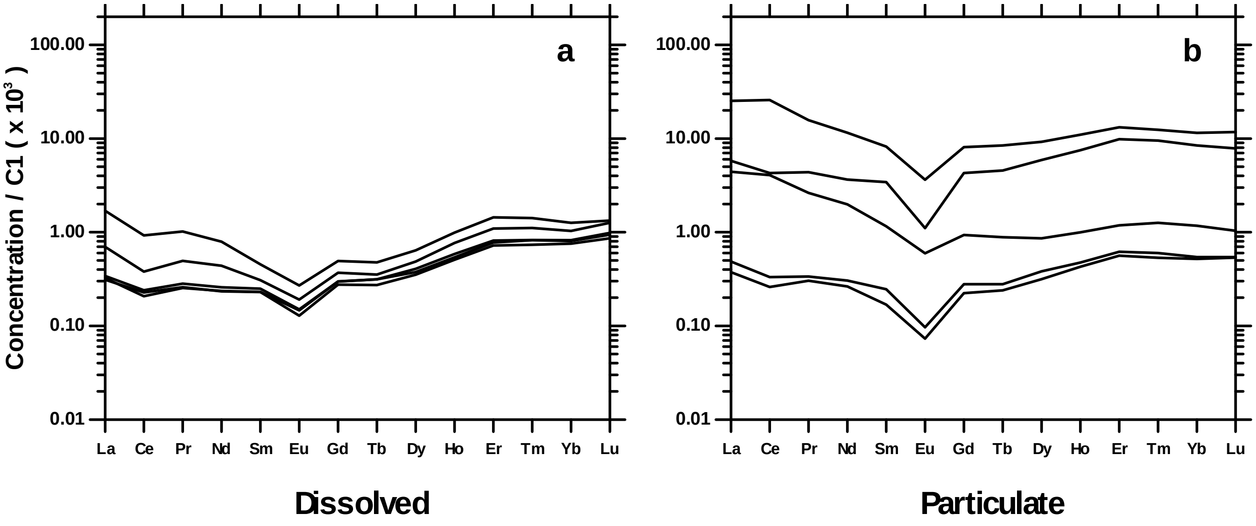

Figure 22: Chondrite-normalized REE patterns for groundwaters from the Amalgamated Rare Earth No. 2 deposit: (a) dissolved concentrations; (b) suspended particulate concentrations. C1-chondrite abundances are from Anders and Grevesse (1989).

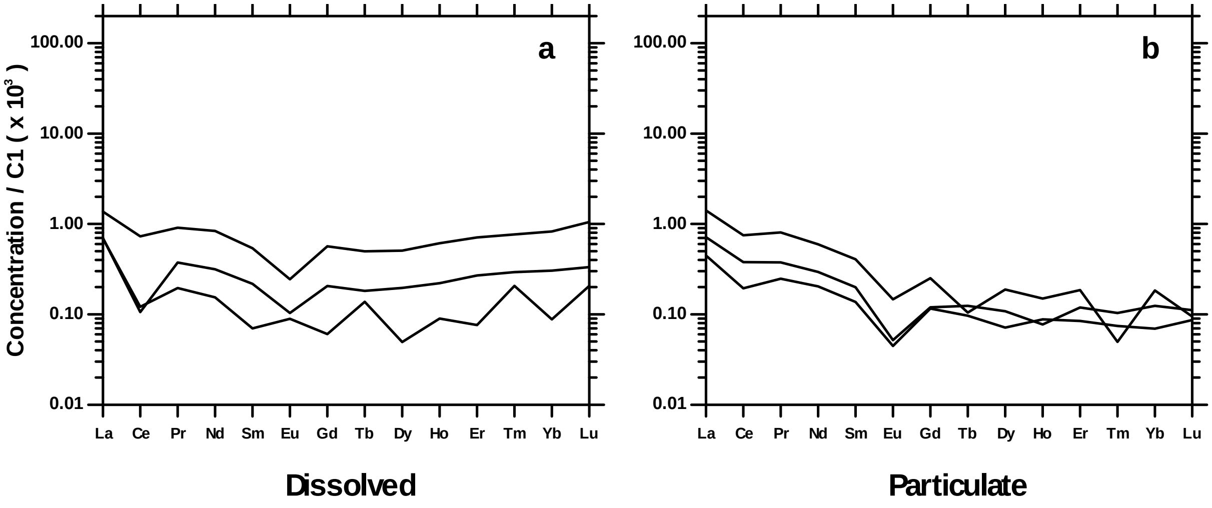

Figure 23: Chondrite-normalized REE patterns for groundwaters from the Halo deposit: (a) dissolved concentrations; (b) suspended particulate concentrations. C1-chondrite abundances are from Anders and Grevesse (1989).

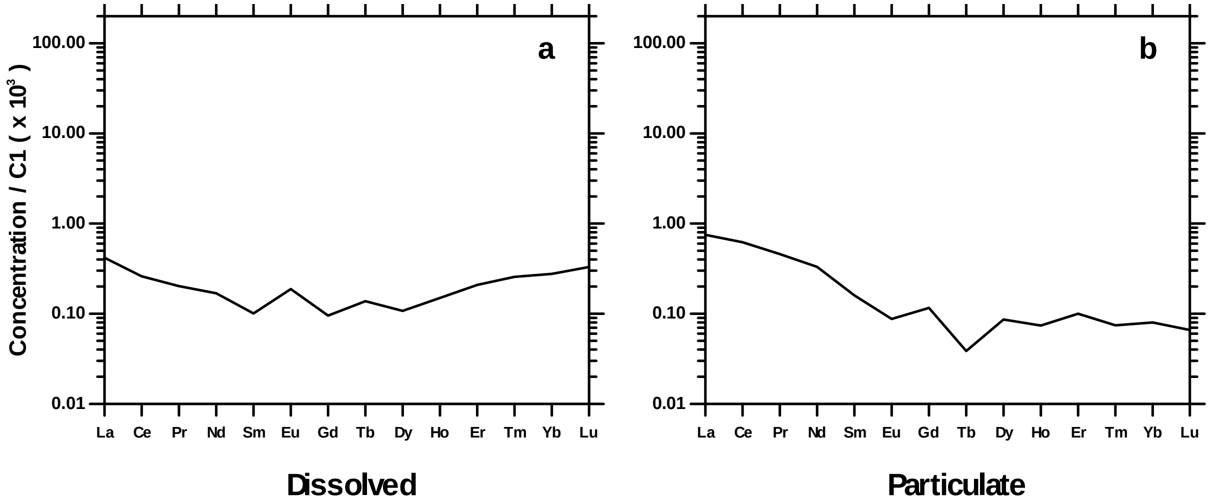

Figure 24: Chondrite-normalized REE patterns for groundwaters from the Canada Radium deposit: (a) dissolved concentrations; (b) suspended particulate concentrations. C1-chondrite abundances are from Anders and Grevesse (1989).

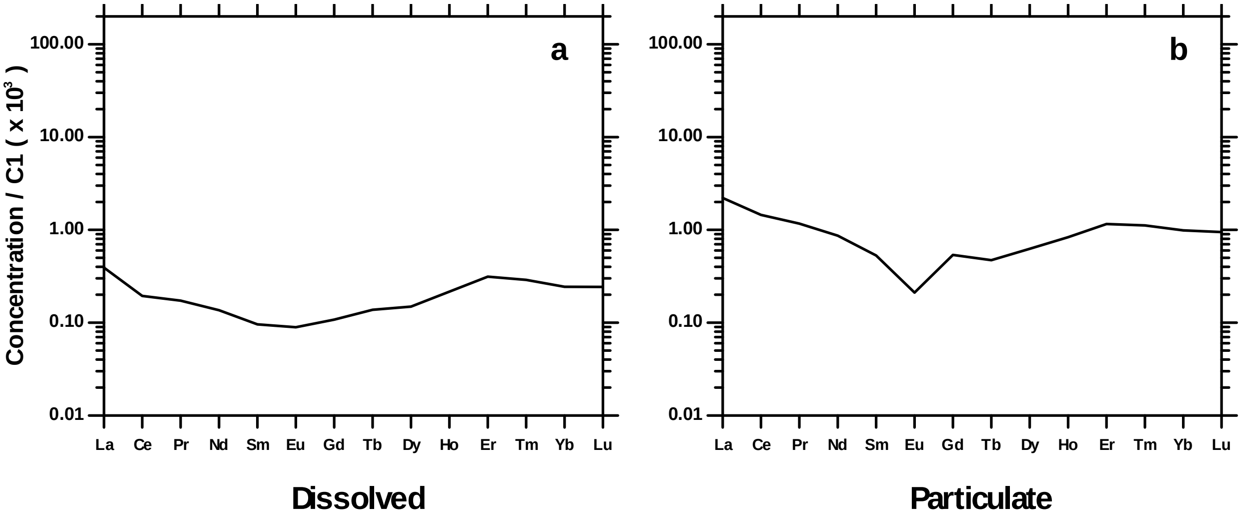

Figure 25: Chondrite-normalized REE patterns for groundwaters from the Saranac deposit: (a) dissolved concentrations; (b) suspended particulate concentrations. C1-chondrite abundances are from Anders and Grevesse (1989).

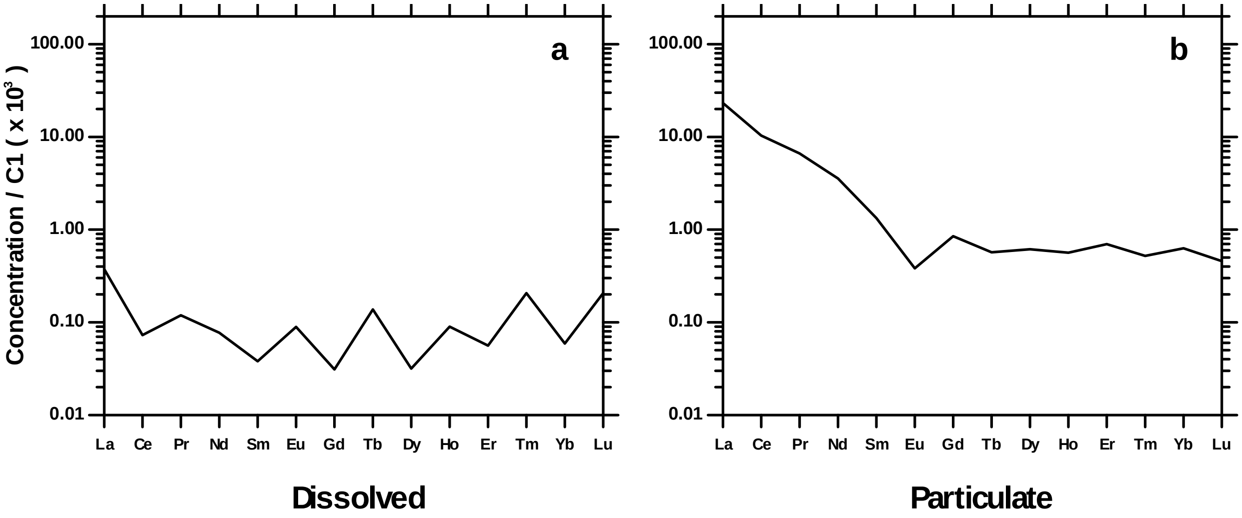

Figure 26: Chondrite-normalized REE patterns for groundwaters from the Amalgamated Rare Earth No.1 deposit: (a) dissolved concentrations; (b) suspended particulate concentrations. C1-chondrite abundances are from Anders and Grevesse (1989).

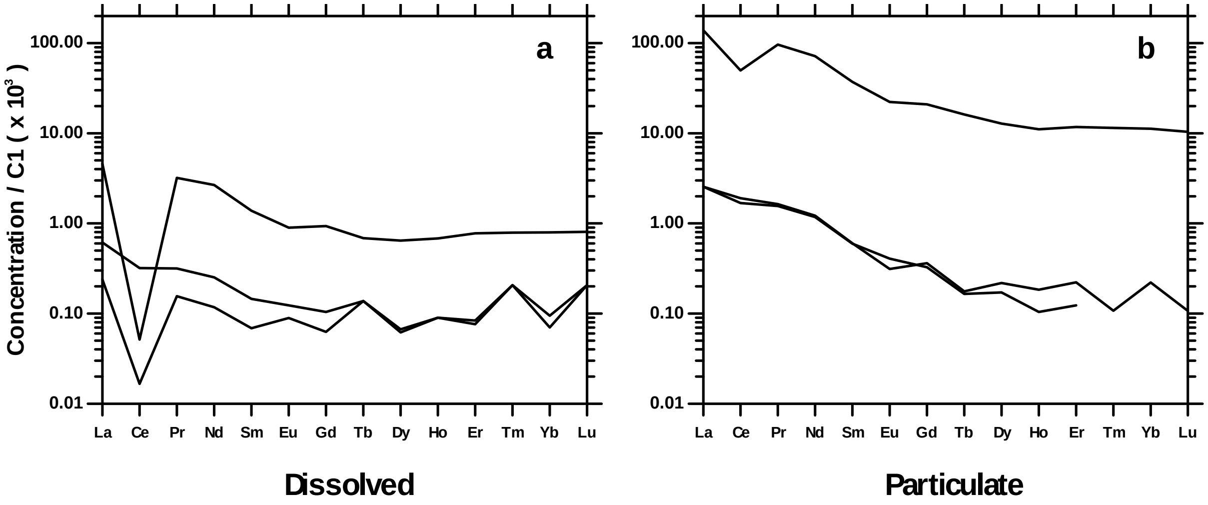

Figure 27: Chondrite-normalized REE patterns for groundwaters from the Canadian All Metals deposit: (a) dissolved concentrations; (b) suspended particulate concentrations. C1-chondrite abundances are from Anders and Grevesse (1989).

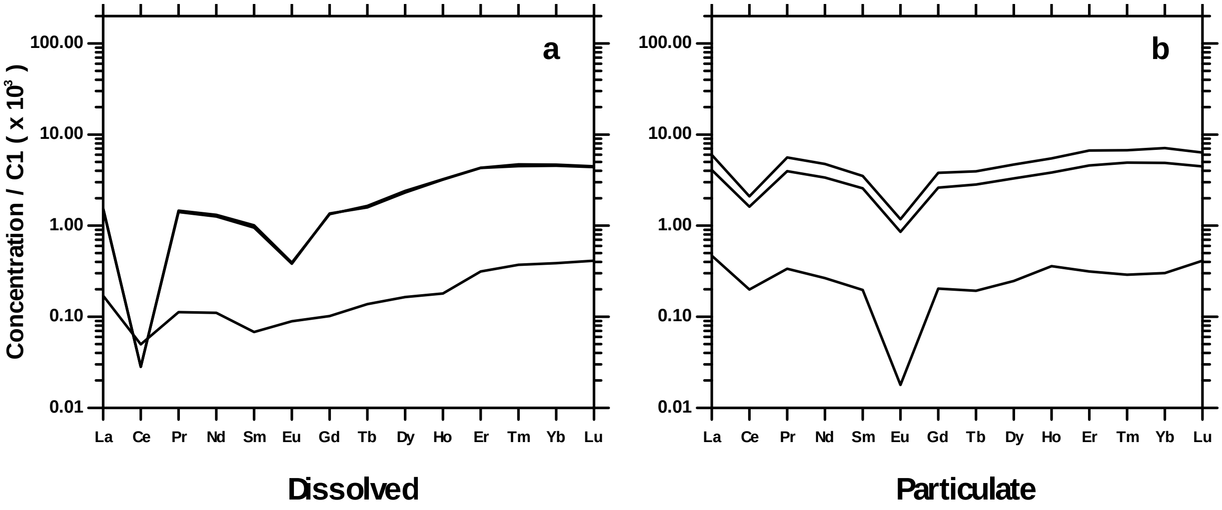

Figure 28: Chondrite-normalized REE patterns for groundwaters from the Silver Crater deposit: (a) dissolved concentrations; (b) suspended particulate concentrations. C1-chondrite abundances are from Anders and Grevesse (1989).

DISCUSSION

Baseline Concentrations of Uranium, Thorium and Rare Earth Elements

This study has purposely focused on groundwaters expected to be anomalous because of their close association with U-Th-REE deposits at various stages of mining development. However, in order to assess the environmental significance of U, Th and REE concentrations reported in this study, they should be compared to natural background concentrations observed in groundwaters from unmineralized yet otherwise similar host rocks. Groundwaters in granitic terrane generally are known to exhibit enriched concentrations of U, Th and REE (Ayotte et al., 2007; Banks et al., 1995, 1999; Lahermo and Juntunen, 1991; Prat et al., 2009).

The Ontario Geological Survey recently completed an extensive survey of groundwater quality in both overburden and bedrock wells throughout southern Ontario (Hamilton, 2015). Geographical coverage was spatially uniform with a sampling density of 1 per 100 km^2. The data set includes groundwater analyses from wells completed in Precambrian gneiss, marble and migmatite to the south and east of the Bancroft area. Trace element concentrations from these wells may be considered representative of natural background values in the study area.

The cumulative distribution of U concentrations from mineral deposits can be compared to that of background values (Figure 29). While the distributions partially overlap, groundwaters from mineral deposits typically exhibit U concentrations greater than background by a factor approaching two orders of magnitude. The Health Canada (2014) MAC for U of 20 µg/L is exceeded in approximately 70% of groundwater samples from mineral deposits and in only 5% of samples from unmineralized bedrock.

The cumulative distributions of Th concentrations in groundwaters from mineralized and unmineralized host rocks are compared in Figure 30. Approximately 65% of samples from unmineralized bedrock have Th concentrations less or equal to the analytical detection limit of 0.001 µg/L. For groundwaters from mineral deposits, approximately 80% of samples have concentrations less or equal to the detection limit of 0.02 µg/L. Despite the different analytical detection limits for the two studies, the data in Figure 30 suggest that Th concentrations in groundwaters associated with mineral deposits are generally higher than background values. Nonetheless, the contrast between Th concentrations from mineralized and unmineralized host rocks appears to decrease at the highest percentile levels.

Cumulative distribution plots for sum of LREE (Figure 31) and sum of HREE (Figure 32) in groundwaters from mineralized and unmineralized host rocks exhibit similar patterns. Concentrations of LREE and HREE from mineral deposits are higher than background values at lower percentiles. However, with increasing percentiles, the distributions of concentrations from mineralized and background populations gradually converge.

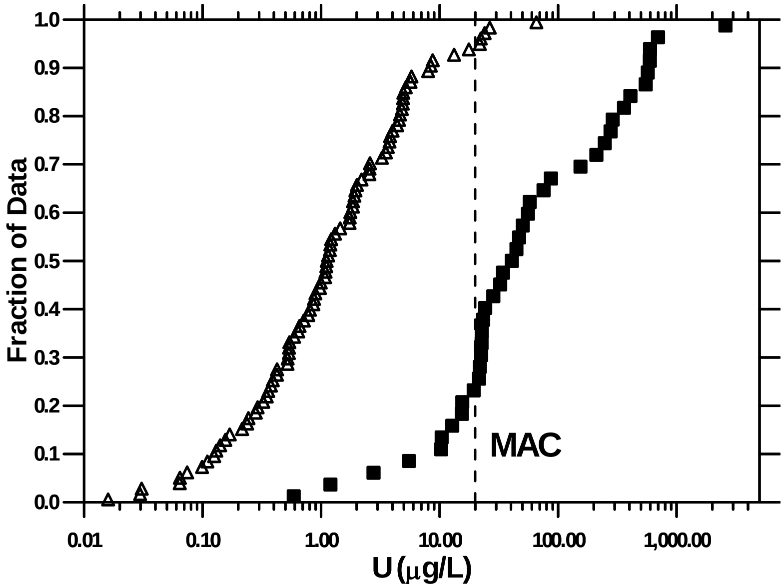

Figure 29: Cumulative distribution plot of filtered U concentrations from mineral deposits sampled in this study (squares) and domestic wells screened in Precambrian bedrock (triangles) from the regional survey of Hamilton (2015). The Health Canada (2014) Maximum Acceptable Concentration (MAC) of 20 μg/L is shown for reference.

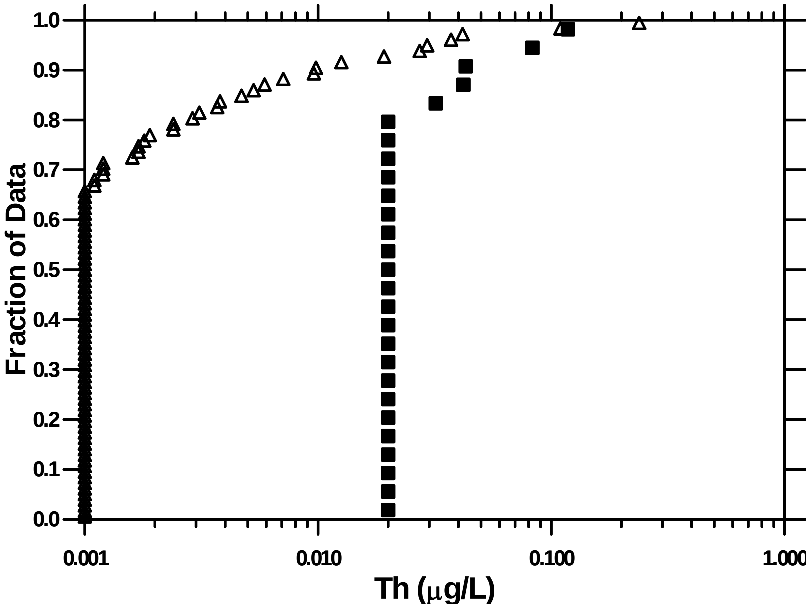

Figure 30: Cumulative distribution plot of filtered Th concentrations from mineral deposits sampled in this study (squares) and domestic wells screened in Precambrian bedrock (triangles) from the regional survey of Hamilton (2015). The analytical detection limits for the two data sets are 0.02 and 0.001 μg/L, respectively.

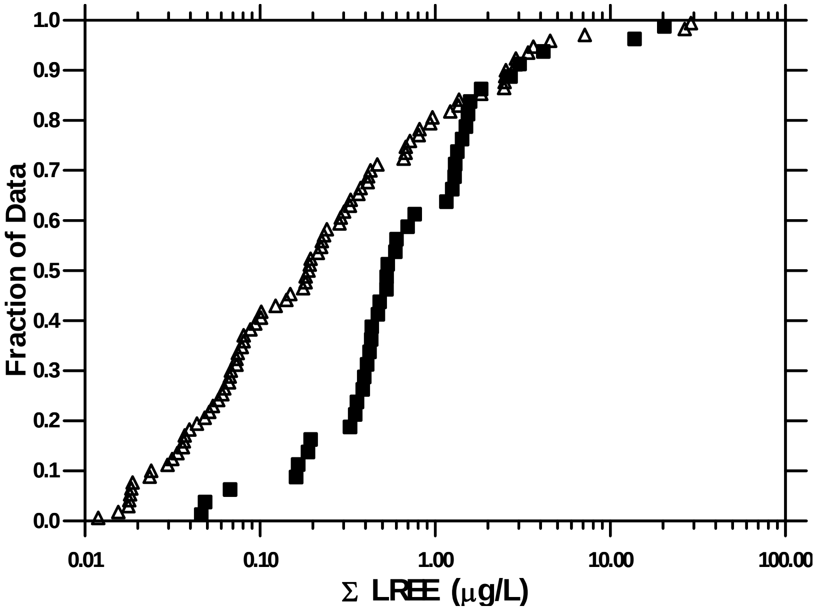

Figure 31: Cumulative distribution plot of the sum of LREE filtered concentrations from mineral deposits sampled in this study (squares) and domestic wells screened in Precambrian bedrock (triangles) from the regional survey of Hamilton (2015).

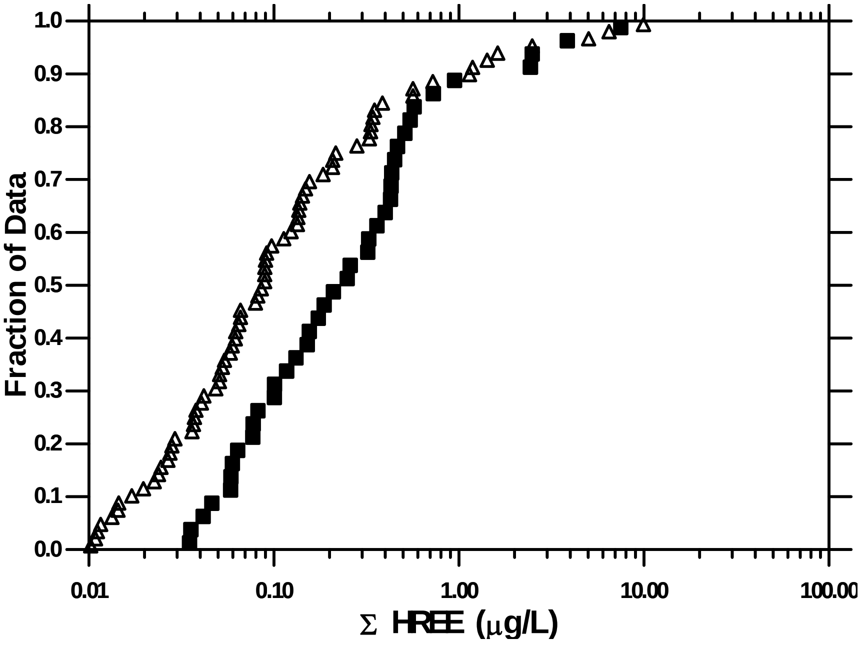

Figure 32: Cumulative distribution plot of the sum of HREE filtered concentrations from mineral deposits sampled in this study (squares) and domestic wells screened in Precambrian bedrock (triangles) from the regional survey of Hamilton (2015).

Table 7: Summary statistics for filtered (< 0.45 µm) concentrations (in µg/L) of U, Th, LREE and HREE in groundwaters from mineral deposits (this study) and from natural background areas (Hamilton, 2015). Thorium concentrations below the detection limit were assigned a value equal to the detection limit. No Th analyses were available for the 2011 samples of this study.

		Mineral Deposits	Natural Background
U	N	40	89
	Minimum	1.2	0.02
	Maximum	2579.7	65.6
	Interquartile Range	240.5	3.4
	Median	42.6	1.1
	Mean	208.4	3.8
	Standard Deviation	434.4	8.5
Th	N	27	89
	Minimum	0.02	0.001
	Maximum	0.12	0.24
	Interquartile Range	0.00	0.001
	Median	0.02	0.001
	Mean	0.03	0.007
	Standard Deviation	0.02	0.03
LREE	N	40	89
	Minimum	0.05	0.01
	Maximum	20.36	28.90
	Interquartile Range	1.01	0.63
	Median	0.53	0.18
	Mean	1.69	1.24
	Standard Deviation	3.75	4.21
HREE	N	40	89
	Minimum	0.03	0.01
	Maximum	7.50	9.94
	Interquartile Range	0.38	0.15
	Median	0.23	0.06
	Mean	0.64	0.42
	Standard Deviation	1.35	1.37

Table 7 and the previous figures show that groundwaters associated with U-Th-REE deposits are enriched in U, Th and REE compared to groundwaters from unmineralized host rocks. However, the ranges of Th, LREE and HREE concentrations associated with mineral deposits fall within ranges observed in unmineralized bedrock. Uranium concentrations associated with mineral deposits, on the other hand, exhibit a much greater range than background values. Their mean is greater than that of background values by a factor of more than 50. As shown in Figure 29, U concentrations from groundwaters associated with mineral deposits are significantly more likely to exceed the Health Canada (2014) MAC of 20 µg/L. The MAC provides a reasonable threshold for distinguishing groundwaters in contact with U-Th-REE mineralization from natural background.

Impact of Mine Drainage on Downstream Surface Waters

The elevated U concentrations observed in groundwaters associated with U-Th-REE deposits suggest that discharge of mine drainage to surface waters could be an environmental concern. In this study, discharge from adit portals was observed (in descending order of U concentration) at the Croft, Amalgamated Rare Earth No.1, Amalgamated Rare Earth No.2, Halo (Lake Zone) and Silver Crater mines. In an unpublished companion study by the Geological Survey of Canada conducted between 2010 and 2012, U concentrations were measured in streams and lakes immediately downstream of these adits. In Figure 33, downstream U concentrations are plotted against corresponding U concentrations measured in portal discharge.

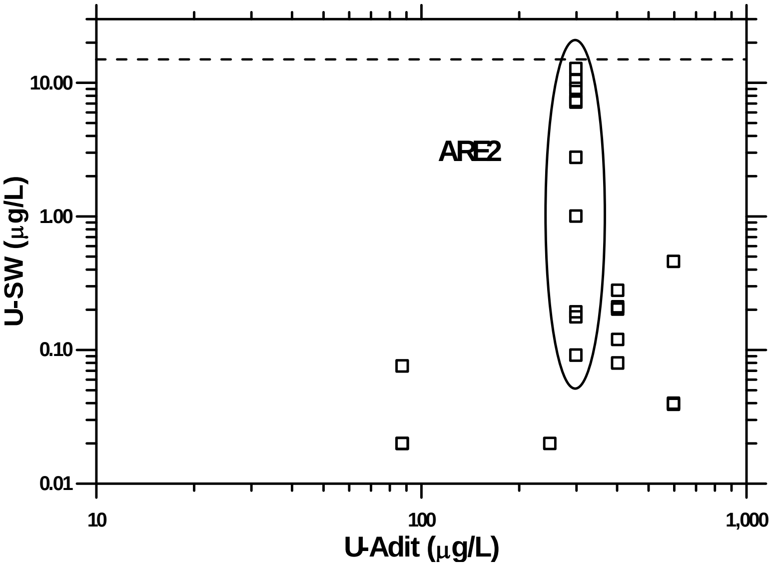

Figure 33: Uranium (total) concentrations observed in surface waters (streams and lakes) downstream of mine adits versus U (total) concentrations observed at five adit portals. The dashed line represents the CCME (2011) guideline for aquatic life of 15 µg/L. Surface water data are from an unpublished companion study. Data for the Amalgamated Rare Earth No. 2 (ARE2) adit are circled.

Data for four of the five adits show a subtle positive correlation between downstream and portal U concentrations (Figure 33) and this likely reflects higher natural background levels in areas of mineralized bedrock. Based on his regional survey, Chamberlain (1964) reported average background concentrations of 1.7, 1.5, and 1.1 µg/L, in creeks, lakes, and swamps, respectively. Here, most surface water concentrations remain below 1 µg/L. Surface waters downstream of the Amalgamated Rare Earth No. 2 portal, on the other hand, are highly anomalous and they exhibit U concentrations approaching the CCME (2011) guideline for aquatic life (15 µg/L).

Drainage from the portal of the Amalgamated Rare Earth No.2 adit flows approximately 120 m beneath a waste rock pile and through a marsh to Lowry Lake (44.9314 ° N, 78.2508 ° W). This headwater lake is surrounded on the north, east, and south by steep knolls of mineralized bedrock. It drains to the west through a short channel to the Irondale River. In addition to adit drainage, it is likely that natural groundwater discharge also contributes U loadings to Lowry Lake. The highest surface water U concentrations are observed in the eastern basin of the lake, opposite the mine workings. Concentrations are lower in the shallow western end of the lake and in the outlet channel.

Chamberlain (1964) also investigated the local distribution of U downstream of the portal at the Amalgamated Rare Earth No.2 mine. He observed elevated concentrations along the flow path to the lake. However, within 3 m of where drainage entered the lake, concentrations decreased to 20 µg/L. The rest of the lake exhibited near-normal background values in the range of 1 to 3 µg/L. The Chamberlain (1964) survey was conducted in 1961, approximately five years after the end of exploration development. The GSC surface water results shown in Figure 33, obtained in 2011, suggest that ongoing adit drainage over fifty five years has resulted in a measurable increase in U concentrations in Lowry Lake.

CONCLUSIONS AND RECOMMENDATIONS

Granitic pegmatite-hosted U-Th-REE deposits and related mineralized skarns and calcite dikes are widespread within the Grenville geological province of eastern Canada. However, mining of such deposits has only taken place in the Bancroft area of Ontario. Renewed exploration for this type of mineral deposit in Ontario and Québec has raised concerns about impacts to groundwater quality. In order to better inform public debate on uranium exploration, government policy, and regulatory decision-making, the Geological Survey of Canada has undertaken a study of groundwater quality at historical mines and prospects in the Bancroft area. Samples were obtained from flooded shafts, flowing adits and diamond drill holes.

Groundwaters associated with U-Th-REE deposits are characterized by low to moderate specific conductance and circum-neutral pH. The main dissolved species are calcium and bicarbonate, mainly from the dissolution of calcite, a ubiquitous accessory mineral. Other important dissolved species include magnesium and sulfate, from the dissolution of ferromagnesian silicate and sulfide minerals, respectively.

Uranium, from the dissolution of uraninite and uranothorite, is the trace element of most environmental concern in groundwaters from these deposits. It was also found to be the most abundant, occurring at concentrations as high as 2580 µg/L. The Health Canada (2014) Maximum Acceptable Concentration (MAC) for U of 20 µg/L was exceeded in approximately 70% of samples. The U is almost entirely in the dissolved (filtered < 0.45 µm) phase with only limited adsorption on hydrous ferric oxides in most samples. The high U mobility observed in this study can be attributed to the availability of dissolved Ca and carbonate species for the formation of stable ternary uranyl complexes known to inhibit adsorption. Redox conditions are another factor that was found to control U mobility. Uranium concentrations were found to be low in more reducing groundwaters characterized by elevated concentrations of dissolved Fe.

Radium-226 (^{226}Ra) and lead-210 (^{210}Pb) are radioactive decay products of ^{238}U, the main isotope occurring in natural uranium. Health Canada (2014) MAC for ^{226}Ra and ^{210}Pb are 0.5 and 0.2 Bq/L, respectively. It was found that groundwaters exhibiting U concentrations less than the MAC of 20 µg/L are unlikely to exhibit Ra and Pb radionuclide activities in excess of their respective regulatory limits.

Thorium is released through the dissolution of (thorian) uraninite and uranothorite along with U. However, mass balance considerations and the stoichiometry of the Th-bearing minerals indicate that Th concentrations in groundwater are not commensurate with observed U values. Most Th is removed from solution close to source through precipitation or adsorption. Maximum Th concentrations of 0.12 µg/L and 11.56 µg/L were observed in filtered and unfiltered groundwater samples, respectively. Thorium occurs mainly the suspended particulate (> 0.45 µm) phase, sorbed on hydrous ferric oxides.

Allanite is a minor accessory mineral in granitic pegmatite U-Th-REE deposits but is likely the main source of light REE (La-Gd) in associated groundwaters. The sources of heavy REE (Tb-Lu) appear to be quite varied and may include betafite and euxenite. Maximum total REE concentrations of 24.2 µg/L and 126.5 µg/L were observed in filtered and unfiltered groundwater samples, respectively. Rare Earth Elements occur mainly the suspended particulate (> 0.45 µm) phase, sorbed on manganese oxyhydroxides. The low REE concentrations reflect the low in-situ abundance of REE-bearing minerals and their generally low solubility.

This study purposely focused on groundwaters expected to be anomalous because of their close association with U-Th-REE mineral deposits at various stages of mining development. However, the environmental significance of U, Th and REE concentrations reported here depends on their contrast with natural background concentrations observed in groundwaters from unmineralized yet otherwise similar host rocks. The Ontario Geological Survey recently completed an extensive survey of groundwater quality in wells throughout southern Ontario (Hamilton, 2015) including wells screened in Precambrian gneiss and marble to the south and east of the Bancroft area. Trace element concentrations in groundwaters from these wells may be considered representative of natural background values within the study area. It was found that the ranges of Th, LREE and HREE concentrations observed in this study fall within the ranges observed in groundwaters from unmineralized Precambrian bedrock, although mean concentrations are somewhat higher. Uranium concentrations, on the other hand, exhibit a much wider range than background values and their mean is more than 50 times greater. The MAC for uranium of 20 µg/L provides a reasonable threshold for distinguishing groundwaters in contact with U-Th-REE mineralization from natural background waters.

The elevated U concentrations observed in groundwaters from U-Th-REE deposits could pose an environmental risk to surface water quality if these groundwaters are discharged from mine workings directly to downstream creeks, lakes and wetlands. Uranium concentrations in portal discharge from five adits were compared to U concentrations observed in surface waters downstream. In four of five cases, natural attenuation processes reduced U concentrations to background levels of approximately 1 µg/L. However, at the Amalgamated Rare Earth No.2 mine, drainage from the adit over the last 60 years has increased U concentrations in adjacent Lowry Lake to values approaching the 15 µg/L guideline for the protection of aquatic life. Further monitoring of water and sediment quality in Lowry Lake is recommended.

This retrospective investigation of environmental impacts to groundwater quality from historical mining activity in the Bancroft district provides basic geoscience knowledge that may be helpful to regulators and proponents of new mining projects in similar geological settings. This knowledge can be used to anticipate and mitigate environmental impacts associated with future resource development thereby ensuring that modern mining practices are employed to further minimize risks to the environment.

REFERENCES

Alexander, R. L., 1986. Geology of Madawaska Mines Ltd., Bancroft, Ontario. In: E. L. Evans (Ed.), Uranium Deposits in Canada, Can. Inst. Mining Metall., Special Vol., 33, 62-69.

Anders, E., Grevesse, N., 1989. Abundances of the elements: Meteoritic and solar. Geochim. Cosmochim. Acta., 53, 197-214.

Asikainen, M., 1981. State of disebquibrium between ^{238}U, ^{234}U, ^{226}Ra and ^{222}Rn in groundwater from bedrock. Geochim. Cosmochim. Acta, 45, 201-206.

ATSDR, 1990. Toxicological profile for thorium. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service, 174p., Atlanta, GA.

Ayotte, J. D., Flanagan, S. M., Morrow, W. S., 2007. Occurrence of uranium and ^{222}radon in glacial and bedrock aquifers in the northern United States, 1993-2003, U.S. Geol. Surv. Sci. Investigations Rep. 2007-5037, 84 p., Reston, Va.

Banks, D., Røyset, O., Strand, T., Skarphagen, H., 1995. Radioelement (U,Th,Rn) concentrations in Norwegian bedrock groundwater. Env. Geol., 25(3), 165-180.

Banks, D., Hall, G., Reimann, C., Siewers, U., 1999. Distribution of rare earth elements in crystalline bedrock groundwaters: Oslo and Bergen regions, Norway. Appl. Geochem., 14, 27-39.

Bernhard, G., Geipel, G., Brendler, V., Nitsche, H., 1996. Speciation of uranium in seepage waters of a mine tailing pile studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS). Radiochim. Acta, 74, 87-91.

Burton, D. M., 1984. The geology of the CAM uranium deposit, Cardiff Township, Ontario, Canada. M.Sc. thesis, Dept. of Geology, Univ. of New Brunswick, Fredericton, NB, 206 p.

Campbell, K. M., Gallegos, T. J., Landa, E. R., 2015. Biogeochemical aspects of uranium mineralization, mining, milling and remediation. Appl. Geochem., 57, 206-235, doi:10.1016/j.apgeochem.2014.07.022.

Canadian Council of Ministers of the Environment (CCME), 2011. Canadian Water Quality Guidelines for the Protection of Aquatic Life – Uranium. http://ceqg-rcqe.ccme.ca/download/en/328/

Carlson, K. A., van der Pluijm, B., Hanmer, S., 1990. Marble mylonites of the Bancroft shear zone: Evidence for extension in the Canadian Grenville. Geol. Soc. Amer., 102, 174-181.

Carson, J. M., Holman, P. B., Ford, K. L., Grant, J. A., Shives, R. B. K., 2004. Airborne gamma ray spectrometry compilation, equivalent uranium, Central Metasedimentary Belt (Grenville

Province), Ontario-Quebec. Geological Survey of Canada, Open File 4559. 1 sheet, doi:10.4095/215115

Carter, T. R., 1984. Metallogeny of the Grenville Province, southeastern Ontario. Ontario Geol. Surv. Open File Rep. 5515, 422 p., Toronto, ON.

Černy, P., Meintzer, R.E., Anderson, A.J., 1985. Extreme fractionation in rare-element granitic pegmatites: Selected examples of data and mechanisms. Can. Mineral., 23, 381-421.

Chamberlain, J. A., 1964. Hydrogeochemistry of uranium in the Bancroft-Haliburton Region, Ontario. Geol. Surv. Canada, Bull. 118, 19 p., Ottawa, ON.

Cothern, R.C., Rebers, P.A., (Eds.), 1990. Radon, radium and uranium in drinking water. Lewis Publishers, 286 p., Chelsea, MI.

Davidson, A., 1998. An overview of Grenville Province geology, Canadian Shield Chapter 3. In: Lucas, S., St-Onge, M. (Eds.) Geology of the Precambrian, Superior and Grenville Provinces and Precambrian Fossils in North America. Geol. Surv. Can., Geology of Canada Series No. 7, 205-270.

Desbarats, A.J., Percival, J.B., Venance, K.E, 2016. Trace element mobility in mine waters from granitic pegmatite U-Th-REE deposits, Bancroft area, Ontario. Appl. Geochem., 67, 153-167.

Easton, R. M., 1992. The Grenville Province and the Proterozoic history of Central and Southern Ontario. In: P. C. Thurston, H. R. Williams, R. H. Sutcliffe, G. M. Stott (Eds.) Geology of Ontario, Ontario Geol. Surv. Spec. Vol. 4, chap. 19, 715-904, Toronto, ON.

Easton, R. M., Fyon, J. A. 1992. Metallogeny of the Grenville Province. In: P. C. Thurston, H. R. Williams, R. H. Sutcliffe, G. M. Stott (Eds.) Geology of Ontario, Ontario Geol. Surv. Spec. Vol. 4, chap. 24, 1217-1252, Toronto, ON.

Ecozones, 2014. The Ecological Framework of Canada. Accessed in 2014 from: http://ecozones.ca

Environment Canada, 2014. Canadian Climate Normals 1981-2010 Station Data. Downloaded from http://climate.weather.gc.ca/climate_normals/

EPA, 2012. Rare Earth Elements: A review of production, processing, recycling, and associated environmental issues. U.S. Environ. Protect. Agency, Office of Research and Development, Rep. EPA/600/R-12/572, Cincinnati, OH.

Focazio, M.J., Szabo, Z., Kraemer, T.F., Mullin, A.H., Barringer, T.H., dePaul, V.T., 2001. Occurrence of selected radionuclides in ground water used for drinking water in the United States: A reconnaissance survey, 1998. U.S. Geol. Surv. Water Resour. Investigations. Rep. 00-4723, 40 p., Reston, VA.

Gascoyne, M., 1989. High levels of uranium and radium in groundwaters at Canada's Underground Research Laboratory, Lac du Bonnet, Manitoba, Canada. Appl. Gechem., 4, 577-591.

Goad, B. E., 1990. Granitic pegmatites of the Bancroft area, southeastern Ontario, Ontario Geol. Surv., Open File Rep. 5717, 459 p., Toronto, ON.

Gordon, J. B., Rybak, U. C., Robertson, J. A., 1981. Uranium and thorium deposits of southern Ontario, Ontario Geol. Surv., Open File Rep. 5311, 665 p., Toronto, ON.

Griffith, J. W., 1986. Uranium deposits of the Bancroft area, Ontario. In: E. L. Evans (Ed.), Uranium Deposits in Canada, Can. Inst. Mining Metall., Special Vol., 33, 57-61.

Grunsky, E. C., Friske, P. W. B., McNeil, R., 2014. A re-evaluation of lake sediment geochemistry from the Bancroft region of Ontario; recognizing geochemical background and sources of uranium and REE mineralization. Geol. Surv. Canada, Open File 7624, 94 p.

Hamilton, S. M., 2015. Ambient groundwater geochemistry data for southern Ontario, 2007-2014. Ont. Geol. Surv., Miscellaneous Release-Data 283-Revised.

Health Canada, 2014. Guidelines for Canadian drinking water quality – Summary Table. Water and Air Quality Bureau, 25 p., Ottawa, ON.

Hewitt, D. F., 1967. Uranium and thorium deposits of southern Ontario. Ontario Dept. Mines, Mineral Res. Circ. No. 4, 76 p., Toronto, ON.

Hornbrook, E. H. W., Lund, N. G., Lynch, J. J., 1984. Geochemical lake sediment and water, southern Ontario, maps and data. Geol. Surv. Canada., Open File 900, 182 p.

Johannesson, K.H. (Ed.), 2004. Rare Earth Elements in Groundwater Flow Systems. Springer, 293 p., Dordrecht.

Kelly, S. D., Kemner, K. M., Brooks, S. C., 2007. X-ray absorption spectroscopy identifies calcium-uranyl-carbonate complexes at environmental concentrations. Geochim. Cosmochim. Acta, 71, 821-834, doi:10.1016/j.gca.2006.10.013.

Laidlow, A. M., Parsons, M. B., Jamieson, H. E., 2015. Characterization of uranium and rare earth element mobility downstream of a tailings impoundment near Bancroft, Ontario. In: Proceedings of the 10th International Conference on Acid Rock Drainage (ICARD) and International Mine Water Association (IMWA) Conference, Santiago, p. 1-10.

Lahermo, P., Juntunen, R., 1991. Radiogenic elements in Finnish soils and groundwaters. Appl. Geochem., 6, 169-183.

Langmuir, D., 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochim. Cosmochim. Acta, 42, 547-569.

Lentz, D., 1991. Radioelement distribution in U, Th, Mo, and rare-earth-element pegmatites, skarns, and veins in a portion of the Grenville Province, Ontario and Quebec. Can. Jour. Earth Sci., 28, 1-12.

Lentz, D., 1992. Petrogenesis and geochemical composition of biotites in rare-element granitic pegmatites in the southwestern Grenville Province, Canada. Mineral. Petrol., 46, 239-256.

Lentz, D., 1996. U, Mo, and REE mineralization in late-tectonic granitic pegmatites, southwestern Grenville Province, Canada. Ore Geology Reviews, 11, 197-227.

Lumbers, S. B., Heaman, L. M., Vertolli, V. M., Wu, T. W., 1990. Nature and timing of Middle Proterozoic magmatism in the Central Metasedimentary Belt, Grenville Province, Ontario. In: Gower, C. F., Rivers, T., Ryan, B. (Eds.) Mid-Proterozoic Laurentia-Baltica, Geol. Assoc. Can., Spec. Pap. 38, 243-276.

Lund, N. G., Hornbrook, E. H. W., Lynch, J. J., 1984. Geochemical lake sediment and water, southeastern Ontario, maps and data. Geol. Surv. Canada., Open File 899, 232 p.

McNeil, R. J., Friske, P. W. B., 2014. New geochemical data from the reanalysis of lake sediment samples with original water data from the Bancroft, Ontario area (parts of NTS 031C, D, E, and F), Geol. Surv. Canada, Open File 7282.

MMER, 2002. Metal Mine Effluent Regulations. Canada Gazette Part II, v.136, no.13, pp. 1246-1543. http://laws-lois.justice.gc.ca/eng/regulations/sor-2002-222/index.html

Ontario Geological Survey (OGS), 1991. Bedrock geology of Ontario, southern sheet. Ont. Geol. Surv., Map 2544, scale 1:1,000,000.

Ontario, 2012. Ontario Radar Digital Surface Model version 1. Water Resources Information Program, Ministry of Natural Resources, Geographic Information Branch, Science and Information Resources Division, Peterborough, ON, 58 p.

Pagano, G., Guida, M., Tommasi, F., Oral, R., 2015. Health effects and toxicity mechanisms of rare earth elements – Knowledge gaps and research prospects. Ecotox. Environ. Safety, 115, 40-48, doi:10.1016/j.ecoenv.2015.01.030.

Parsons, M. B., Friske, P. W. B., Laidlow, A. M., Jamieson, H. E., 2014. Controls on uranium, rare earth element and radionuclide mobility at the decommissioned Bicroft Uranium Mine, Ontario. Geol. Surv. Canada., Sci. Presen. 24, 1 sheet, doi:10.4095/293623

Peterson, R. C., MacFarlane, D. B., 1993. The rare-earth-element chemistry of allanite from the Grenville Province. Can. Mineral., 31, 159-166.

Prat, O., Vercouter, T., Ansoborlo, E., Fichet, P., Perret, P., Kurttio, P., Salonen, L., 2009. Uranium speciation in drinking water from drilled wells in southern Finland and its potential links to health effects. Environ. Sci. Technol., 43, 3941-3946, doi:10.1021/es803658e.

Proulx, M., 1997. The uranium mining industry of the Bancroft area: an environmental history and heritage assessment. M.A. thesis, Faculty of Arts and Science, Trent University, 157 p., Peterborough, ON.

Richardson, D. G., Birkett, T. C., 1996. Peralkaline rock-associated rare metals. In: Eckstrand, O.R., Sinclair, W.D., Thorpe, R.I. (Eds.) Geology of Canadian Mineral Deposit Types. Geology of Canada Series, No. 8, 523-540, Geol. Surv. Can., Ottawa, ON.

Rimsaite, J., 1982. Mineralogical and petrochemical properties of heterogeneous granitoid rocks from radioactive occurrences in the Grenville Structural Province, Ontario and Quebec. In: Maurice, Y.T. (Ed.) Uranium in Granites, Geol. Surv. Canada, paper 81-23, 19-30.

Robinson, S.C. and Sabina, A.P., 1955. Uraninite and thorianite from Ontario and Quebec, Amer. Mineral., 40, 624-633.

Robinson, S. C., and Abbey, S., 1957. Uranothorite from eastern Ontario. Can. Mineral., 6, 1-15.

Rogers, J. J., Ragland, P. C., Nishimori, R. K., Greenberg, J. K., Hauck, S. A., 1978. Varieties of granitic uranium deposits and favorable exploration areas in the Eastern United States. Econ. Geol., 73, 1539-1555.

Sabina, A. P., 1986. Rocks and minerals for the collector, Bancroft – Parry Sound area and Southern Ontario. Geol. Surv. Canada, Misc. Rep. 39, 182 p., Ottawa, ON.

Satterly, J., 1957. Radioactive mineral occurrences in the Bancroft area. Ontario Dept. Mines, 65th Ann. Rep., Part 6, 1956, 176 p., Toronto, ON.

Smedley, P. L., 1991. The geochemistry of rare earth elements in groundwater from the Carnmenellis area, southwest England. Geochim. Cosmochim. Acta, 55, 2767-2779.

Strong, W.L., Zoltai, S.C., Ironside, G.R., 1989. Ecoclimatic regions of Canada, Ecological Land Classification Series 23, Canadian Wildlife Service, Environment Canada, Ottawa, 122 p.

Szabo, Z., Zapecza, O.S., 1991. Geologic and geochemical factors controlling uranium, radium-226, and radon-222 in ground water, Newark Basin, New Jersey. In: Gundersen, L.C.S., and Wanty, R.B. (Eds.), Field Studies of Radon in Rocks, Soils, and Water. U.S. Geol. Surv., Bull. 1971, 243-265.

Wanty, R.B., Schoen, R., 1991. A review of the chemical processes affecting the mobility of radionuclides in natural waters, with applications. In: Gundersen, L.C.S., and Wanty, R.B. (Eds.), Field Studies of Radon in Rocks, Soils, and Water. U.S. Geol. Surv., Bull. 1971, 183-194.

Wiken, E.B. 1986. Terrestrial Ecozones of Canada. Ecological Land Classification, Series No. 19. Environment Canada. Hull, Quebec. 26 pp. and map.