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**GEOLOGICAL SURVEY OF CANADA  
OPEN FILE 7282**

**New geochemical data from the re-analysis of archived lake  
sediment samples including original water data from the  
Bancroft, Ontario area  
(Parts of NTS 31-C, -D, -E and -F)**

**R.J. McNeil and P.W.B. Friske**

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# **New geochemical data from the re-analysis of archived lake sediment samples including original water data from the Bancroft, Ontario area (Parts of NTS 31-C, -D, -E and -F)**

## **Introduction**

New analytical data for 65 elements from the re-analysis of archived lake sediment samples collected from 362 sites in the Bancroft, Ontario area, in 1976 and 1982 are presented in this Geological Survey of Canada (GSC) open file (OF) release. Field observations with accompanying sediment and water analytical data originally reported in GSC Open Files 899 (Lund et al., 1984) (preceded by OF 405 (Hornbrook et al., 1977a) and OF 406 (Hornbrook et al., 1977b)) and OF 900 (Hornbrook et al., 1984) are included in this report.

Analytical results and field observations from this project form part of a national geochemical database used for resource assessment, mineral exploration, geological mapping, and environmental studies. Sample collection, preparation procedures and analytical methods are strictly specified and carefully monitored to ensure consistent and reliable results regardless of the area, the year of collection or the analytical laboratory undertaking the analyses.

Re-analysis of archived samples provides data for an extended set of elements as well as improved, lower detection limits for many elements at approximately five percent of the cost of collecting new samples. Historical samples represent a unique time stamp and cannot truly be re-sampled; however re-analysing them creates new data for uptake in a variety of applications. Analysis by modern techniques makes the results from samples taken decades ago directly comparable to analyses of newly acquired samples. Measurements of historical samples support comparison and interpretation of temporal changes. Creating new analytical results from archived samples allows a fuller range of geochemical data to evaluate temporal trends and to quantify historical baseline concentrations.

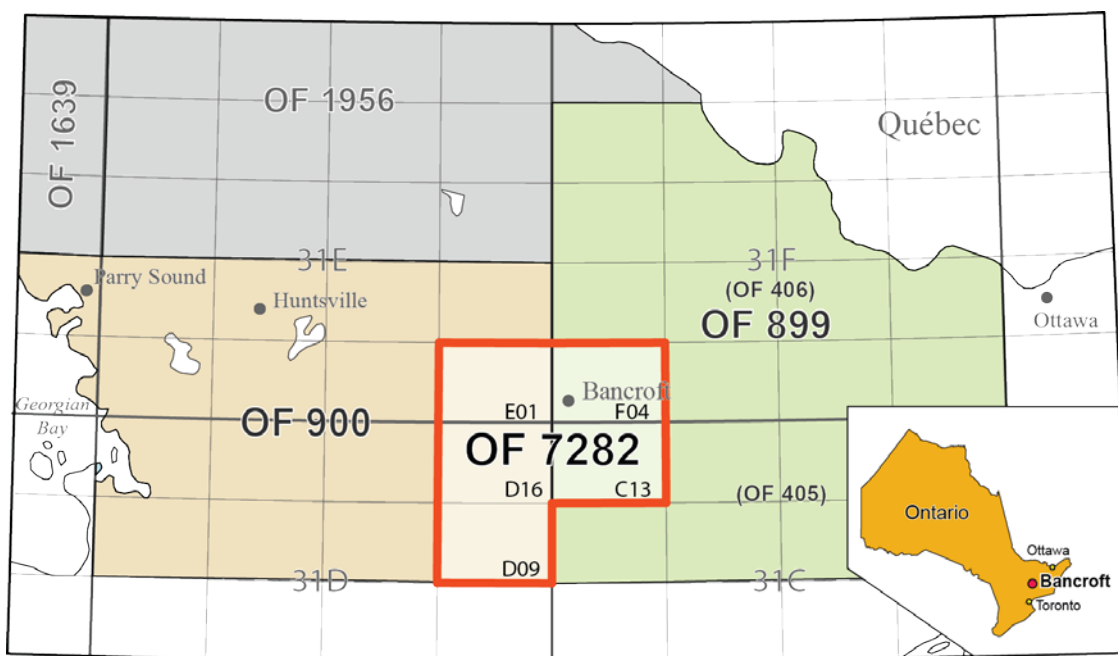


Figure 1. Map showing area where OF 7282 sediment samples were selected for re-analysis in the Bancroft, ON area.

Shown in Figure 1 is an outline of the area where a subset of samples was re-analysed. These samples were stored in a GSC archive facility in Ottawa and were originally collected in 1976 (OF 899 – previously OF 405 and 406) and 1982 (OF 900) under the former Federal-Provincial Uranium Reconnaissance Program.

The Uranium Reconnaissance Program was designed to provide industry with high quality reconnaissance exploration data and to provide the Federal Government with nationally systematic data for undertaking uranium resource appraisals. Re-analysis of archive samples were supported by the Earth Science Sector's Environmental Geoscience Program (EGP) at Natural Resources Canada (NRCan) for new applications.

The Bancroft geo-environmental Uranium-Rare Earth Element (U-REE) model activity is part of the Tools for Environmental Impact Assessment for the Metal Mining project under the EGP, which is a 5-year investment by the Government of Canada. Specifically, this 5-year activity will develop a geo-environmental model for U-REE deposits in the Grenville Geological Province to support sustainable development of new mineral resources and to predict the sources, transport and fate of contaminants, as well as develop protocols to assess background conditions in regions subject to mineral development.

### Description of Survey and Sample Management

In 1975, the GSC completed a geochemical orientation study in the Faraday, Cardiff and Monmouth area. These data were never published and are being compiled for release as a separate GSC Open File. As a follow-up, in 1976 the National Geochemical Reconnaissance (NGR) group at the GSC carried out two lake sediment surveys (not surface water) covering NTS sheets 31C and 31F. Data were published in Open File 405 and 406 respectively. In 1982, an adjacent lake sediment and water survey, covering NTS sheets 31D and 31E, was carried out and results were published in GSC Open File 900. Also in 1982, most original sites from OF 405 and 406 were revisited to collect water samples. The new water data were combined with the original sediment data from Open Files 405 and 406 and were published as Open File 899 (refer to Table 1). The sediment samples collected in 1976 were also re-analysed by additional methods similar to Open File 900 and included in Open File 899 (Table 1)

**Table 1** Summary of sample collection and analysis of the data presented in this open file.

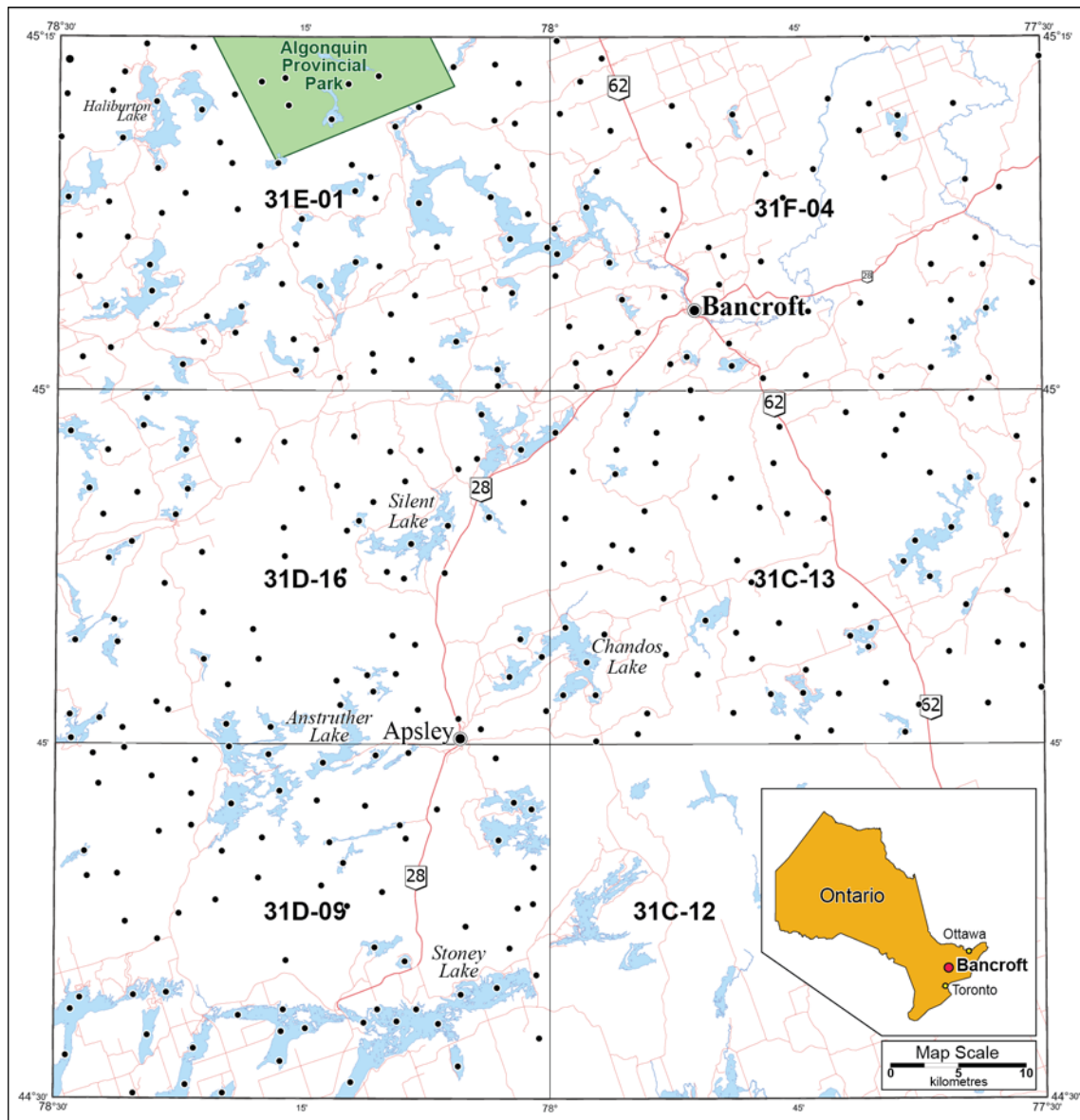
Open File #	405	406	899 *	900	7282 **
Year of Collection	1976	1976	1976 (sed) & 1982 (water)	1982	1976 & 1982
NTS	31C	31F	31C & F	31D & E	31C13, 31D09 & 16, 31E01 and 31F04
Total Sediment Sites	580	769	1132	1033	362
Total Water Sites	0	0	1132	1033	350
<b>Sediment Analysis</b>	<b>Year</b>	<b>Year</b>	<b>Year</b>	<b>Year</b>	<b>Year</b>
AAS, CV-AAS, NADNC, LOI (500°C)	1976	1976	-	1982	-
XRF, LOI (900°C), LECO, Titration	-	-	1982	1982	-
<b>Water Analysis</b>					
pH, Temp, Cond., DO, AAS, LIF, IC, ISE, Alkalinity	-	-	1982	1982	-
<b>Sediment subset for re-analysis (362 samples)</b>					
ICP-MS (Aqua Regia) - year	-	-	-	-	2012
ICP-MS (4-acid) - year	-	-	-	-	2012

\* Republished original 1976 sediment data only where a water sample was collected from revisited sites in 1982 (1132 of 1349 original sites were revisited).

\*\* Re-analysed subset of 362 samples covering NTS sheets 031C13, 031D09 & 16, 031E01 and 031F04. Includes all previous datasets listed above. Water samples collected in 1982 (OF899), when revisiting sites from OF405 and 406, were labelled differently than the original 1976 sediment sample (OF405 and 406). This open file refers to those water samples with the original corresponding sediment sample number reported in OF405 and 406. The water sample number was added in the data file for reference only.

For the purpose of this study, a subset of 362 sediment samples, covering parts of both OF899 and 900 (NTS 31C13, 31D09 & 16, 31E01 and 31F04) (Figure 2), was retrieved from the NGR sample archive and re-analysed by two different methods: 1) aqua-regia digestion followed by inductively coupled plasma-mass spectrometry (ICP-MS) and 2) a 4-acid digestion followed by ICP-MS analyses. All original data associated with these samples from OF899 and 900 as well as these new data from re-analysis are compiled

in this report. The 362 sample sites from which sediments were re-analysed for this report (Figure 2) are distributed throughout the 5,470 km<sup>2</sup> area, at an average density of one sample per 15 km<sup>2</sup>. A sample location map is included [here](#) as .pdf format with sample numbers as well as a .kmz format for [Google Earth](#).



**Figure 2.** Map showing locations of the lake sediment samples re-analysed and water samples in the Bancroft, ON area.

A bottom-valved, hollow-pipe sampler (Figure 3) was used to collect approximately one kilogram of wet lake sediment by penetrating the sediment approximately 20-25 cm. Field observations for each site were recorded on standard forms (Figure 4) used by the GSC. See Garrett, 1974 for complete descriptions of the field card. At GSC laboratories in Ottawa, samples were air-dried and sieved through an 80 mesh (177 µm) screen before milling in ceramic-lined puck mills. Typically, one kilogram of wet organic gel, the preferred lake sediment sample material, yielded about 50 g of material for analysis. After milling, control reference and blind duplicate samples were inserted into each block of twenty sample numbers. For quality control purposes, the original samples were arranged in groups (consecutively-numbered blocks) of twenty. Each group of twenty samples contained site duplicates; that is, two samples from a single site. The group also contained an analytical duplicate sample pair (a single site sample split and assigned two non-consecutive sample numbers). Finally, each group included a control reference sample. Before publication, thorough inspections of the field and analytical data were made to check for any missing information and/or analytical errors. A

[illegible]

## Analytical Procedures (2012)

Samples were re-analysed by ICP-MS with two different digestion methods prior to analysis.

The first dissolution was a modified aqua-regia "partial" dissolution using package 1F-04 at ACME Analytical Laboratories, Limited, Vancouver, British Columbia. Fifty three elements are determined and lower detection limits are summarized in Table 2. Pulp-splits of 0.5-g samples were leached with a 6-ml mixture of HCl, HNO<sub>3</sub>, and distilled/deionized water (1:1:1 volume to volume ratio) at 95°C for one hour. The sample solution was diluted to 20 ml and analysed by ICP-MS (Perkin-Elmer Elan instrument).

**Table 2.** Elements determined by aqua-regia ICP-MS for re-analysis of archive lake sediment samples.

Element	Detection Limit	Units of Measurement	Analytical Method
Ag	2	PPB <sup>1</sup>	ICP-MS
Al	0.01	PCT <sup>2</sup>	ICP-MS
As	0.1	PPM <sup>3</sup>	ICP-MS
Au	0.2	PPB	ICP-MS
B	20	PPM	ICP-MS
Ba	0.5	PPM	ICP-MS
Be	0.1	PPM	ICP-MS
Bi	0.02	PPM	ICP-MS
Ca	0.01	PCT	ICP-MS
Cd	0.01	PPM	ICP-MS
Ce	0.1	PPM	ICP-MS
Co	0.1	PPM	ICP-MS
Cr	0.5	PPM	ICP-MS
Cs	0.02	PPM	ICP-MS
Cu	0.01	PPM	ICP-MS
Fe	0.01	PCT	ICP-MS
Ga	0.1	PPM	ICP-MS
Ge	0.1	PPM	ICP-MS
Hf	0.02	PPM	ICP-MS
Hg	5	PPB	ICP-MS
In	0.02	PPM	ICP-MS
K	0.01	PCT	ICP-MS
La	0.5	PPM	ICP-MS
Li	0.1	PPM	ICP-MS
Mg	0.01	PCT	ICP-MS
Mn	1	PPM	ICP-MS
Mo	0.01	PPM	ICP-MS

Element	Detection Limit	Units of Measurement	Analytical Method
Na	0.001	PCT	ICP-MS
Nb	0.02	PPM	ICP-MS
Ni	0.1	PPM	ICP-MS
P	0.001	PCT	ICP-MS
Pb	0.01	PPM	ICP-MS
Pd	10	PPB	ICP-MS
Pt	2	PPB	ICP-MS
Rb	0.1	PPM	ICP-MS
Re	1	PPB	ICP-MS
S	0.02	PCT	ICP-MS
Sb	0.02	PPM	ICP-MS
Sc	0.1	PPM	ICP-MS
Se	0.1	PPM	ICP-MS
Sn	0.1	PPM	ICP-MS
Sr	0.5	PPM	ICP-MS
Ta	0.05	PPM	ICP-MS
Te	0.02	PPM	ICP-MS
Th	0.1	PPM	ICP-MS
Ti	0.001	PCT	ICP-MS
Tl	0.02	PPM	ICP-MS
U	0.1	PPM	ICP-MS
V	2	PPM	ICP-MS
W	0.1	PPM	ICP-MS
Y	0.01	PPM	ICP-MS
Zn	0.1	PPM	ICP-MS
Zr	0.1	PPM	ICP-MS

<sup>1</sup> PPB: parts per billion, µg/kg

<sup>2</sup> PCT: percent, %

<sup>3</sup> PPM: parts per million, mg/kg

## 2- ICP-MS (4-acid dissolution)

The 4-acid dissolution method is a "near total" dissolution using HCl, HNO<sub>3</sub>, HClO<sub>4</sub> and HF mixed in the ratio of 2:2:1:1. Elements determined and lower detection limits are summarized in Table 3. Pulp splits of 0.25 grams were weighed into Teflon test tubes. A 10 ml aliquot of the acid solution was added, heated until fuming on a hot plate and taken to dryness. A 4 ml aliquot of 50% HCl was added to the residue and heated using a mixing hot block. After cooling, the solutions were transferred to polypropylene test tubes and made to a 10 ml volume with 5% HCl. This method is effectively a total dissolution for most elements, although for some (e.g., Cr, Ba, Al, Fe, Al, Hf, Mn, Sn, Ta and Zr) it may only be partial depending on sample mineralogy. Also volatilization during fuming may result in some loss of As, Sb and Au. Analyses were carried out at Acme Analytical Laboratories, Limited, Vancouver, British Columbia.



**Table 3.** Elements determined by 4-acid "near total" dissolution ICP-MS for re-analysis of archive lake sediment samples.

Element	Detection Limit	Units of Measurement	Analytical Method
Ag	20	PPB <sup>1</sup>	ICP-MS
Al	0.02	PCT <sup>2</sup>	ICP-MS
As	0.2	PPM <sup>3</sup>	ICP-MS
Au	100	PPB	ICP-MS
Ba	1	PPM	ICP-MS
Be	1	PPM	ICP-MS
Bi	0.04	PPM	ICP-MS
Ca	0.02	PCT	ICP-MS
Cd	0.02	PPM	ICP-MS
Ce	0.02	PPM	ICP-MS
Co	0.2	PPM	ICP-MS
Cr	1	PPM	ICP-MS
Cs	0.1	PPM	ICP-MS
Cu	0.02	PPM	ICP-MS
Dy	0.1	PPM	ICP-MS
Er	0.1	PPM	ICP-MS
Eu	0.1	PPM	ICP-MS
Fe	0.02	PCT	ICP-MS
Ga	0.02	PPM	ICP-MS
Gd	0.1	PPM	ICP-MS
Hf	0.02	PPM	ICP-MS
Ho	0.1	PPM	ICP-MS
K	0.02	PCT	ICP-MS
La	0.1	PPM	ICP-MS
Li	0.1	PPM	ICP-MS
Lu	0.1	PPM	ICP-MS
Mg	0.02	PCT	ICP-MS
Mn	2	PPM	ICP-MS

Element	Detection Limit	Units of Measurement	Analytical Method
Mo	0.05	PPM	ICP-MS
Na	0.002	PCT	ICP-MS
Nb	0.04	PPM	ICP-MS
Nd	0.1	PPM	ICP-MS
Ni	0.1	PPM	ICP-MS
P	0.001	PCT	ICP-MS
Pb	0.02	PPM	ICP-MS
Pr	0.1	PPM	ICP-MS
Rb	0.1	PPM	ICP-MS
S	0.04	PCT	ICP-MS
Sb	0.02	PPM	ICP-MS
Sc	0.1	PPM	ICP-MS
Sm	0.1	PPM	ICP-MS
Sn	0.1	PPM	ICP-MS
Sr	1	PPM	ICP-MS
Ta	0.1	PPM	ICP-MS
Tb	0.1	PPM	ICP-MS
Th	0.1	PPM	ICP-MS
Ti	0.001	PCT	ICP-MS
Tm	0.1	PPM	ICP-MS
U	0.1	PPM	ICP-MS
V	1	PPM	ICP-MS
W	0.1	PPM	ICP-MS
Y	0.1	PPM	ICP-MS
Yb	0.1	PPM	ICP-MS
Zn	0.2	PPM	ICP-MS
Zr	0.2	PPM	ICP-MS

<sup>1</sup> PPB: parts per billion, µg/kg

<sup>2</sup> PCT: percent, %

<sup>3</sup> PPM: parts per million, mg/kg

#### **Analytical Procedures (1976 & 1982)** (*descriptions taken from original open files 405, 406, 899 & 900*)

Analytical procedures for sediment analysis are summarized in Table 4 and procedures for water analysis are summarized in Table 5.

#### ***Sediment Analyses***

For the determination of Ag, As, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn, a 1 gram sample was reacted with 6 ml of a mixture of 4M HCl and 1M HNO<sub>3</sub> in a test tube overnight at room temperature. After the overnight digestion, the test tube was immersed in a hot water bath at room temperature and brought up to 90°C and held at this temperature for 2 hours with periodic shaking. The sample solution was then diluted to 20 ml with metal free water and mixed. Ag, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn were determined by atomic absorption spectroscopy (AAS) using an air-acetylene flame. Background corrections were made for Pb, Ni, Co, Ag and Cd.

**Mo** and **V** were determined by AAS using a nitrous oxide acetylene flame. A 0.5 gram sample was reacted with 1.5 ml concentrated HNO<sub>3</sub> in a test tube overnight at room temperature. After digestion, the test tube was immersed in a hot water bath at room temperature, brought up to 90°C, and held at this temperature for 30



minutes with periodic shaking. At this point, 0.5 ml concentrated HCl was added and the digestion continued at 90°C for an additional 90 minutes. After cooling, 8 ml of a 1,250 ppm Al solution was added and the sample solution diluted to 10 ml before aspiration.

**Hg** was determined by the Hatch and Ott procedure with some modifications. The method is described by Jonasson et al. (1973). A 0.5 gram sample was reacted with 20 ml concentrated HNO<sub>3</sub> and 1.0 ml concentrated HCl in a test tube for 10 minutes at room temperature prior to two hours of digestion with mixing at 90° C in a hot water bath. After digestion, the sample solutions were cooled and diluted to 100 ml with metal-free water. The Hg present was reduced to the elemental state by the addition of 10 ml weight per volume (w/v) SnSO<sub>4</sub> in 1 M H<sub>2</sub>SO<sub>4</sub>. The Hg vapour was then flushed by a stream of air into an absorption cell mounted in the light path of an atomic absorption spectrophotometer. Absorption measurements were made at 253.7 nm.

**LOI (500°C)** was determined using a 0.5 gram sample. The sample, weighed into a 30 ml beaker, was placed in a cold muffle furnace and brought up to 500°C over a period of two to three hours. The sample was held at this temperature for four hours then allowed to cool to room temperature for weighing.

**LOI (900°C)** was determined using a 0.5 gram sample. The sample, weighed into a 30 ml beaker, was placed in a cold muffle furnace and brought up to 900°C over a period of two to three hours. The sample was held at this temperature for four hours then allowed to cool to room temperature for weighing.

**Organic carbon** was determined by performing a loss on ignition measurement at 450°C after evolution of water. Lake sediments had organic carbon levels much too high for conventional organic carbon methods.

**As** was determined by atomic absorption using a hydride evolution method wherein the arsenic was evolved as AsH<sub>3</sub>, passed through a heated quartz tube in the light path of an atomic absorption spectrophotometer. This method was described by Aslin (1976).

**CO<sub>2</sub>** was evolved by treating a sample with HCl and absorbing the evolved CO<sub>2</sub> in Ba(OH)<sub>2</sub> solution. Measurement was made by back-titrating excess Ba(OH)<sub>2</sub> with 0.1M HCl and phenolphthalein as the indicator.

**U** was determined using a neutron activation method with delayed neutron counting. A detailed description of this method was provided by Boulanger et al. (1975). In brief, a 1 g sample was weighed into a 7-dram polyethylene vial, capped and sealed. The samples were pneumatically transferred from an automatic loader to a 'Slowpoke' reactor, where each sample was irradiated for 20 seconds in an operating flux of 10<sup>12</sup> neutrons/cm<sup>2</sup>/sec. After irradiation, the samples were transferred to a counting facility where, after a ten second delay, each sample was counted for 20 seconds with six BF<sub>3</sub> detector tubes embedded in paraffin wax. Following counting, samples were ejected into a shielded storage container. Analysis of uranium in lake sediments was carried out at Atomic Energy of Canada, Limited (AECL), Ottawa, Ontario.

**S** was determined by the X-ray fluorescence pressed disc method. The sample was mixed with an organic binder and pressed into a pellet in a hydraulic press. The pellet was then taken to an X-ray fluorescence spectrophotometer for analysis and the results calculated by a mini-computer.

**Rb, Sr, Cr, Zr, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, MnO, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> and BaO** were determined by mixing the sample with lithium metaborate, lithium fluoride and ammonium nitrate, fusing in a Claisse® Fluxer, pouring into a mold and the resulting disc read by X-ray fluorescence spectrometry and calculations done by a mini computer.

**Table 4.** Summary of determined variables and the methods used for sediment sample analysis in 1976 and 1982.

Element	Detection Limit	Units of Measurement	Analytical Method	Year of analysis
Ag	200	PPB <sup>1</sup>	AAS <sup>a</sup>	1976 & 1982
As	1.0	PPM <sup>2</sup>	AAS	1976 & 1982
Cd	0.2	PPM	AAS	1982
Co	2	PPM	AAS	1976 & 1982
Cu	2	PPM	AAS	1976 & 1982
Fe	0.02	PCT <sup>3</sup>	AAS	1976 & 1982
Hg	10	PPB	CV-AAS <sup>b</sup>	1976 & 1982
Mn	5	PPM	AAS	1976 & 1982
Mo	2	PPM	AAS	1976 & 1982
Ni	2	PPM	AAS	1976 & 1982
Pb	2	PPM	AAS	1976 & 1982
V	5	PPM	AAS	1982
Zn	2	PPM	AAS	1976 & 1982
U	0.5	PPM	NADNC <sup>c</sup>	1976 & 1982
LOI (500°C)	1.0	PCT	Grav <sup>d</sup>	1976
LOI (900°C)	0.2	PCT	Grav	1982
C-Org	0.2	PCT	LECO (450°C)	1982
CO <sub>2</sub>	0.2	PCT	Titration	1982
S	0.02	PCT	XRF <sup>e</sup>	1982
Al <sub>2</sub> O <sub>3</sub>	0.1	PCT	XRF-LiBO <sub>2</sub> <sup>f</sup>	1982
BaO	0.02	PCT	XRF-LiBO <sub>2</sub>	1982
CaO	0.1	PCT	XRF-LiBO <sub>2</sub>	1982
Cr	10	PPM	XRF-LiBO <sub>2</sub>	1982
Fe <sub>2</sub> O <sub>3</sub>	0.1	PCT	XRF-LiBO <sub>2</sub>	1982
K <sub>2</sub> O	0.1	PCT	XRF-LiBO <sub>2</sub>	1982
MgO	0.05	PCT	XRF-LiBO <sub>2</sub>	1982
MnO	0.02	PCT	XRF-LiBO <sub>2</sub>	1982
NaO <sub>2</sub>	0.1	PCT	XRF-LiBO <sub>2</sub>	1982
P <sub>2</sub> O <sub>5</sub>	0.02	PCT	XRF-LiBO <sub>2</sub>	1982
Rb	20	PPM	XRF-LiBO <sub>2</sub>	1982
SiO <sub>2</sub>	1	PCT	XRF-LiBO <sub>2</sub>	1982
Sr	20	PPM	XRF-LiBO <sub>2</sub>	1982
TiO <sub>2</sub>	0.02	PCT	XRF-LiBO <sub>2</sub>	1982
Zr	10	PPM	XRF-LiBO <sub>2</sub>	1982

<sup>1</sup> PPB: parts per billion, µg/kg    <sup>2</sup> PPM: parts per million, mg/kg    <sup>3</sup> PCT: percent, %

<sup>a</sup> AAS: Atomic Absorption Spectroscopy

<sup>b</sup> CV-AAS: Cold Vapour - Atomic Absorption Spectroscopy

<sup>c</sup> NADNC: Neutron activation – Delayed Neutron Counting

<sup>d</sup> Grav: Gravimetric Methods

<sup>e</sup> XRF: X-Ray fluorescence

<sup>f</sup> XRF-LiBO<sub>2</sub>: LiBO<sub>2</sub> fusion by X-Ray fluorescence

### Water analyses

**Zn, Mn, Fe, Na, K, Ca and Mg** in lake water were determined by atomic absorption spectrophotometry using an air-acetylene flame on a fully automated Perkin-Elmer 5000. Cesium was used as the ionization buffer (1000 µg/ml) for Na, K, Ca and Mg. Lanthanum was used as a releasing agent (2000 µg/ml) for Ca and Mg.

**U** in lake water was determined by laser-induced fluorometry with the Scintrex UA-3. A 500 µl aliquot of the metaphosphate-pyrophosphate “Fluran” buffer was added to 5 ml of the sample and left to equilibrate for 24 hours. The fluorescence of the uranyl phosphate formed was measured by the method of standard additions following a nullification of any signal from organic fluorescence.

**pH** - Hydrogen ion activity was measured using a Radiometer TTT81.

**Organic carbon** in lake water was measured using a Barnstead Analyser based on conductimetric analysis. The CO<sub>2</sub> contribution from inorganic species was zeroed out after acidification and the increase in conductivity was measured after liberation of CO<sub>2</sub> by oxidation with ultra-violet irradiation and potassium persulphate.

**Cl, Br, NO<sub>3</sub>, SO<sub>4</sub> and PO<sub>4</sub>** in lake water were determined by ion chromatography/conductimetric analysis using a fully automated DIONEX Model 12 chromatograph. The samples were initially filtered through 0.45 µm Millipore filter paper and injected onto the columns. An anion exchange resin was used as a separator, followed by a high capacity cation-exchange resin as a suppressor in an effluent of 0.0024 M NaHCO<sub>3</sub>/0.003 M Na<sub>2</sub>CO<sub>3</sub>. A chart recorder was used to check the peaks for possible interference.

**Alkalinity (CaCO<sub>3</sub>)** was determined by automatically titrating an aliquot of sample against 0.01 M H<sub>2</sub>SO<sub>4</sub> from the pH of the sample end-point, calculated by the micro-processor on the Radiometer TTT81.

**F** in lake water was determined by adding an aliquot of the sample to a buffer (Tisab) solution and the mv reading of the resulting mixture measured after a delay of 10 minutes with a combination Orion ion-selective electrode.

**Water temperature, conductivity and dissolved oxygen** were determined by the use of a Martek Mark V instrument, a general purpose, multi-parameter, portable water analyser. The instrument measures in-situ temperature, conductivity, dissolved oxygen and pH with automatic temperature compensation for pH and dissolved oxygen. It can be powered by an internal or external battery or 115V power line.

**Table 5.** Summary of determined variables and the methods used for water sample analysis in 1982.

Element	Detection Limit	Units of Measurement	Analytical Method	Year of analysis
Water Temp	-	°C <sup>1</sup>	Martek V <sup>a</sup>	1982
Conductivity	-	µmho/cm <sup>2</sup>	Martek V	1982
Diss. Oxygen	-	PPM <sup>3</sup>	Martek V	1982
pH	-	-	Radiometer TTT82 <sup>b</sup>	1982
U_w	0.02	PPB <sup>4</sup>	LIF <sup>c</sup>	1982
Ca_w	0.2	PPM	AAS <sup>d</sup>	1982
Fe_w	20	PPB	AAS	1982
K_w	0.2	PPM	AAS	1982
Mg_w	0.2	PPM	AAS	1982
Mn_w	10	PPB	AAS	1982
Na_w	0.2	PPM	AAS	1982
Zn_w	5.0	PPB	AAS	1982
Br_w	0.2	PPM	IC <sup>e</sup>	1982
Cl_w	0.05	PPM	IC	1982
NO <sub>3</sub> _w	0.2	PPM	IC	1982

Element	Detection Limit	Units of Measurement	Analytical Method	Year of analysis
PO <sub>4</sub> _w	0.2	PPM	IC	1982
SO <sub>4</sub> _w	0.2	PPM	IC	1982
CaCO <sub>3</sub> _w	0.2	PPM	Titration	1982
F_w	40	PPB	ISE <sup>f</sup>	1982
C-org_w	0.2	PPM	Cond <sup>g</sup>	1982

<sup>1</sup> °C: degree Celsius

<sup>2</sup> mho/cm: ohms/cm

<sup>3</sup> PPM: parts per million, mg/kg

<sup>4</sup> PPB: parts per billion, µg/kg

<sup>a</sup> Martek V: Field instrument

<sup>b</sup> Radiometer TTT82: Field instrument

<sup>c</sup> LIF: Laser-Induced Fluorometry

<sup>d</sup> AAS: Atomic Absorption

Spectroscopy

<sup>e</sup> IC: Ion Chromatography

<sup>f</sup> ISE: Ion-Selective Electrode

<sup>g</sup> Cond: Conductimetric Analysis with Barnstead Analyzer

## Data Files

Field observations and analytical data included with this report are presented in Excel® spreadsheet files (/OF7282/DataFiles.XLSX/). Printer-ready versions are also included as Portable Document Format (PDF) files (/OF7282/DataFiles.PDF/).

**Table 6.** Summary of data files included in this open file report.

<u>Data File</u>	<u>Contents</u>
<b>1- Original_Field Data</b>	Site specific field observations including geographic coordinates (lat/long – NAD83).
<b>2- Original_Aqua-regia - AAS_Sediment</b>	<b>Original 1976 and 1982 Sediment Data - AAS</b> analytical data and summary statistics for lake sediment samples.
<b>3- Original_Additional Analysis_Sediment</b>	<b>Original 1976 and 1982 Sediment Data - NADNC,</b> AAS and other specific analytical methods data and summary statistics for lake sediment samples.
<b>4- Original_AAS and additional Analysis_Water</b>	<b>Original 1982 Water Data - AAS, IC</b> and other specific analytical methods data and summary statistics for water samples.
<b>5- New_Aqua-regia - ICP-MS _Sediment</b>	<b>Re-analysis of sediment samples by aqua-regia dissolution (ICP-MS) Data -</b> aqua-regia analytical data and summary statistics for selected lake sediment samples.
<b>6- New_4-acid - ICP-MS _Sediment</b>	<b>Re-analysis by 4-acid dissolution (ICP-MS) Data -</b> 4-acid analytical data and summary statistics for selected lake sediment samples.

## QUALITY CONTROL OF GEOCHEMICAL RESULTS

The reliability (accuracy and precision) of analytical data returned from commercial laboratories was monitored by incorporating field duplicates (FD pairs) within the sampling protocol and Certified Reference Materials (CRM) within the sample suite submitted to the laboratories. Small sample weights from the original archived samples did not permit analytical ('blind') duplicate sample splits to be included.

For statistical analysis, values below the lower analytical detection limit, were halved for calculation purposes (i.e.  $\leq 200$  ppm  $\Rightarrow$  100 ppm).

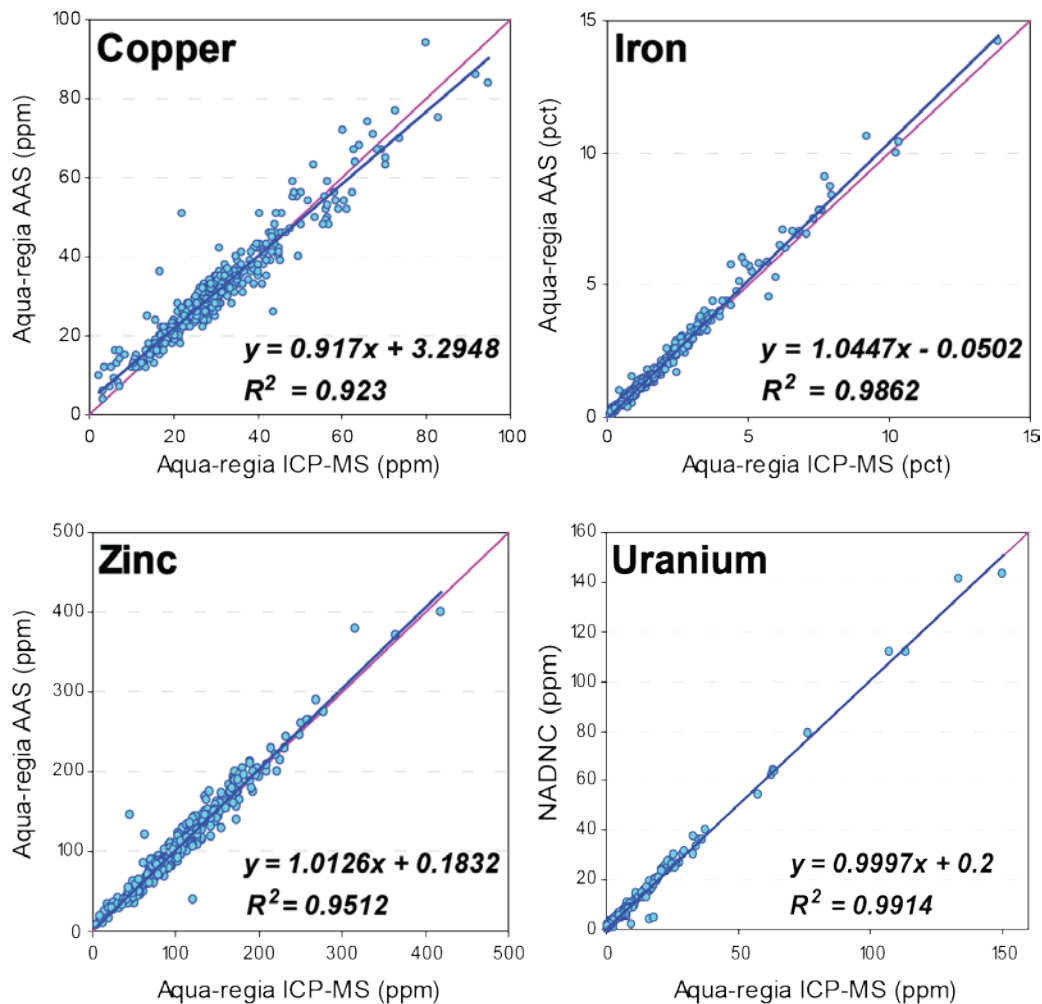


Figure 5. X-Y plots of the original aqua-regia by AAS data versus the re-analysis of aqua-regia by ICP-MS for Cu, Fe, Zn and U. There is a strong correlation between the two datasets with copper being the lowest with an  $R^2$  value of 0.923.

## QUALITY CONTROL DATA FILES

Table 7 below provides information on the number of each quality control sample type included within the sample suite.

**Table 7.** Total number of Certified Reference Material (CRM) and field duplicate pairs (FD pairs) included within the reanalysed sample suite.

Lake sediment samples (N = 362)		
CRM		FD pairs
LKSD-1	LKSD-4	21
10	10	

Analytical data for field duplicate pairs and Certified Reference Material (CRM) are included with this report in Appendices 1 to 4 (refer to Table 8). Data quality was evaluated in a two-step process using CRMs to evaluate precision and accuracy as well as field duplicates to carry out Analyses of Variance (ANOVA) in order to assess fitness-of-purpose ('Are analytical differences between sample sites real?') for mapping.

Appendices are presented in Excel® spreadsheet files (/OF7282/Appendices.XLSX/).

**Table 8.** Summary of appendices. (/OF7282/Appendices/ )

<u>List of Appendices</u>	<u>Contents</u>
<b>Appendix 1_CRM - Analytical Data</b>	Analytical data for Certified Reference Materials LKSD-1 and LKSD-4.
<b>Appendix 2_CRM - Precision and Accuracy</b>	Table of calculated estimates for precision and accuracy of Certified Reference Materials LKSD-1 and LKSD-4.
<b>Appendix 3_Field Duplicate Pairs - Analytical Data</b>	Analytical data of field duplicate pairs.
<b>Appendix 4_Field Duplicate Pairs – ANOVA</b>	Table of calculated simple pair ANOVA estimate proportions of total variability due to each of sampling and analysis.

### *Precision and Accuracy*

Precision and accuracy of the re-analysed data were calculated by evaluating the analytical data of the inserted Certified Reference Materials lake sediments LKSD-1 and LKSD-4 (Appendix 1). LKSD-1 is a combination of lake sediments from two lakes located in central Ontario (Brady Lake, 31M and Joe Lake, 31F). Sediment from three lakes, Big Gull Lake (31C) in Ontario and Key Lake and Seahorse Lake (74H) in Saskatchewan, were combined to prepare LKSD-4 (Lynch, 1990 and 1999).

### *Certified Reference Material*

Appendix 2 lists all the elements determined for CRM LKSD-1 and LKSD-4 by each analytical method with their respective lower detection limits. Along with the data generated as part of this study (Project Values), the table includes the recommended values (mean and standard deviations) published by Lynch (1990 and 1999) and unpublished values from other GSC projects.

### Description of fields in Appendix 2\_CRM - Precision and Accuracy.xlsx

**Analytical Method:** AR (aqua-regia) and 4A (4-acid)

**Recommended values: from Lynch 1990 and 1999**

**Mean:** Published mean value of individual element for each Certified Reference Material.

**Standard Deviation:** Published standard deviation value of individual element for each Certified Reference Material.

**Project values:**

**Total Samples <LDL:** Number of samples where the analytical value is below the lower detection limit. \* <LDL values are halved for calculation of statistics.

**Range (min – max):** Range of analytical values for each element.

**Mean:** Mean of all reported values for each element.

**Standard Deviation:** Standard Deviation of all reported values for each element.

**% RSD:** Relative Standard Deviation expressed as a percentage.

**% Recovery:** Ratio of the mean analytical value to the recommended value for each element expressed as a percentage.

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Most project element means were within an acceptable 2 standard deviations of the recommended mean. The recommended means and associated standard deviations were taken, when available, from Lynch (1990 and 1999). Otherwise, values (highlighted in light green) were derived from unpublished CRM data ( $n \geq 40$ ) collected from recent projects at the GSC. Elements of possible concern, as indicated by a relatively high ( $> 33\%$ ) Percent Relative Standard Deviation (%RSD), are shown in bold type. In many cases, the relatively high %RSD, indicating poor repeatability, was related to elemental values that were close to the lower detection limit.

### **Analysis of Variance (ANOVA)**

Precision and accuracy are ‘external’ criteria against which geochemical survey data are evaluated. In order to establish that these data are ‘fit for purpose,’ an Analysis of Variance (ANOVA) is required (Reimann et al., 2008). Appendix 4\_Field Duplicate Pairs - ANOVA shows results from an ANOVA undertaken on field duplicate pairs. The analytical data used for the calculation of the ANOVA are included in Appendix 3\_Field Duplicate Pairs – Analytical Data.

#### **Field Duplicates**

A one-way random effects model ANOVA was undertaken on each element in a set of 21 field duplicate pairs, representing one field duplicate within each block of 20 sequential sample numbers, to estimate, as a percentage, how much of the total variability was due to sampling and analysis of a lake (‘within’) and how much can be attributed to regional variability across the survey area (‘between’). Results are shown in Appendix 4\_Field Duplicate Pairs – ANOVA.xlsx. Data were not log-transformed because in all but one case (Au), the range of observations did not exceed 1.5 orders of magnitude. The sampling variability was estimated from field duplicates using the ‘anova2’ function in the ‘rgr’ package running under the R system, a random effects ANOVA model estimating whether the combined sampling and analytical variability between duplicate pairs was significantly smaller than the variability between sample sites (Garrett, 2011).

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#### **Description of Worksheet: 4-ANOVA (FD).xlsx**

##### **Percentage of Variation:**

\* **Between Sites:** ANOVA value for the analytical variation *Between Sites* in percentage.

\* **Within Individual Sites:** ANOVA value for the analytical variation *Within Individual Sites* in percentage.

**F-test:** Is a variance ratio to gauge whether the variance ‘*within individual sites*’ is significantly smaller than the variation ‘*between sites*’. As a ‘rule of thumb’ this ratio should exceed 4.0 for sampling and analytical errors to be significantly smaller at the 95% confidence level.

**p-Value:** Is a measure of the exact level of confidence in the results. Generally an acceptable p-value is less than 0.05 ( $>95^{\text{th}}$  percentile), i.e. there is a  $<5\%$  probability the observed F ratio could have occurred due to chance alone.

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### **SINGLE ELEMENT MAPS**

Included in this report is a stand-alone series of 21 elemental map layouts using re-analysed data by 4-acid ICP-MS and LOI by gravimetry. The individual layouts include a proportional dot map, a grid map, summary statistics tables and statistical graphs. The proportional dot maps were produced in MapInfo



Professional and the grid maps with Vertical Mapper, an add-in package to MapInfo Professional. The summary statistics table and statistic graphs were generated with ioGAS. The following table is a list of selected single element map layouts by 4-acid ICP-MS included in this report.

**Table 9.** List of individual single element layout maps with statistics included in this report.

Al	As	Ca	Ce	Co	Cu	Fe
Hg	La	LOI (Grav)	Mn	Mo	Nb	Ni
P	Pb	Rb	Th	U	Y	Zn

## ACKNOWLEDGEMENTS

E.H. Hornbrook directed the original survey carried out in 1976, coordinating the activities of contracted and Geological Survey of Canada staff. Contracts for sample preparation and analysis were managed by J.J. Lynch, GSC.

Quality control of data was carried out with the assistance of Robert Garrett, GSC *Emeritus* Research Scientist. Stephen Day and Sam Alpay of the GSC reviewed this open file and provided useful comments and suggestions to enhance the document.

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