



## **Bedrock and soil geochemistry from Voyageurs National Park, Minnesota**

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## **INTRODUCTION**

Bedrock, forest floor, and mineral soil sampling in Voyageurs National Park (VNP), Minnesota in 2000 and 2001 is part of a multidisciplinary project that includes the U. S. Geological Survey, National Park Service, University of Wisconsin – La Crosse, Minnesota Pollution Control Agency, and the Minnesota Department of Natural Resources. The joint project is examining the distribution of mercury in age-1 perch, lake water, bedrock and soils for eighteen watersheds in the interior of VNP. The purpose of the project was to establish the background and baseline geochemistry for bedrock and soil in the region, and to determine terrestrial mercury sources and sinks in VNP.

## **BEDROCK GEOLOGY**

Bedrock in VNP consists of Late Archean age rocks of the Superior Province. The Rainy Lake-Seine River fault occurs in the very northern part of the Park, separating the Wabagoon subprovince on the north from the Quetico subprovince on the south (Day and others, 1990). Minor gold mineralization is found on several small islands in Rainy Lake along the tectonized margin of the fault. The host rock is mylonitic schist (Day, 1990), and gold typically is found in quartz, associated with pyrite, arsenopyrite, and ankerite. A short-lived gold rush in the late 1890's resulted in numerous small excavations and the building of a stamp mill on the mainland near the largest deposit on Little America Island. Mercury was used in the processing of ore in the stamp mill, and tailings were released into Rainy Lake, just outside Park boundaries.

Rocks of the Quetico subprovince in the northern part of the Park are fine- to medium grained schist and graywackes (Day and others, 1990). Several small leucogranite and dioritic intrusions cut the metasediments. In the southern and eastern part of the Park metasediments grade into schist-rich migmatites and then into more granite-rich migmatite. Large areas of pink to gray biotitic, massive to weakly foliated Lac La Croix granite are predominant in the eastern end of the Park (Day and others, 1990). Rocks correlative with bedrock in the Park have been dated from 2750 to 2500 Ma (Goldich and Peterman, 1980).

## **GLACIAL GEOLOGY**

Multiple episodes of glaciation have covered northern Minnesota. Following retreat of the last ice sheets, the area was inundated by Glacial Lake Agassiz, which probably last drained out of the VNP region by 9700 B.P. (Clayton and Moran, 1982). Deposits of Lake Agassiz lake clay and glacial till and outwash from two disparate Late Wisconsin glacial lobes derived from two different ice centers are found in VNP (Sado and others, 1995). Bedrock in the western third of the Park is covered by ground moraine that is part of the Erskine moraine of the Des Moines lobe (Hobbs and Goebel, 1982). Des Moines lobe tills were derived from shales and limestones in the lowlands of Manitoba, and are generally clayey and carbonate-rich, occasionally with limestone clasts. Overlying bedrock in the eastern two-thirds of the Park are thin glacial deposits of the Vermillion moraine that is part of the Rainy lobe. The Rainy lobe is derived from rocks of the Superior Province, a greenstone-granite terrane. As a result, glacial deposits in the Vermillion moraine are sandy and stony with little clay (Hobbs and Goebel, 1982).

## METHODS OF STUDY

### Sample Collection

Geochemical sample media include rocks and different soil horizons ([Figure 1](#)). Rock samples were collected from outcrop and from the gold mine dump on Little America Island. Rock samples were typically composite chip samples or single grab samples collected at each site. Rock descriptions were recorded in the field and are included in the rock data file.

Soil sample sites were selected for different criteria. Most samples were collected within the watersheds of the lakes investigated in the multidisciplinary study. Within each watershed, attempts were made to collect from both upland and lowland (but not wetland) sites. Several sites outside of the studied watersheds were collected to extend the sampling area to include all available bedrock types and deposits from the two glacial lobes. Additional soil samples were collected from areas that had been burned recently by either prescribed or natural fires.

Soil samples were collected from soil pits hand dug with a shovel and extended with a hand auger. Sample pits were completed to the C-horizon or to a depth dictated by the presence of impenetrable rock. From each soil pit, soil from different horizons, including O-, A-, E- or C-horizons, was collected so that each sample site has multiple geochemical analyses, each representing a different soil layer.

The O-horizon is the organic matter that lies on top of a mineral soil. The organic layer is divided into Oi (forest litter), Oe (forest duff) and Oa (humus) horizons. Forest litter is undecomposed, identifiable dead plant material. Forest duff is partially decomposed organic material that may underlie the litter layer. Humus is completely decomposed, non-identifiable organic material. At each soil sample site, Oe-horizon material was collected, if available. Field descriptions discriminate between undecomposed forest litter and more decomposed forest duff, but do not attempt to distinguish duff from humus. Forest litter was collected at only five sites. Samples from Oe-horizons typically were grab samples collected from the soil plug removed from the sample pit. Litter material, when collected, was composited from material in the area of the sample site.

The A-horizon is the upper layer of mineral soil. Typically the A-horizon has accumulated organic carbon and is distinguished from underlying soil horizons by a change in color. An E-horizon is a zone of eluviation, which is easily distinguished by its light, buff or gray color. A-horizon soils were collected at each sample site, with material composited from the entire thickness of the horizon. A limited number of E-horizon samples were also collected from sample sites.

Subsoil samples collected from the C-horizon typically were composed of weathered parent material, which, in VNP, is either bedrock or thin glacial deposits on bedrock. The depth of collection was typically constrained by the depth to bedrock.

## **Sample Preparation**

All samples were shipped to the USGS analytical laboratories in Denver, CO for sample preparation. Methods for sample preparation for analysis are described here and in more detail in Arbogast (1996).

### ***Rocks***

Rocks were crushed to 0.5 cm fragments in a jaw crusher and fed into a ceramic plate pulverizer where fragments were reduced to approximately minus 100-mesh. Each pulverized sample was split, with a portion submitted for geochemical analysis and a portion archived. Clean quartz rock and sand was crushed and pulverized between samples to eliminate cross-contamination.

### ***Soils***

O-horizon soils were air-dried and milled. Samples were split with one portion set aside for mercury analysis and the remainder of the sample ashed at 500 °C and submitted for analysis. Percent ash is calculated as:

$$\% \text{ ash} = (\text{ashed sample weight} / \text{unashed sample weight}) \times 100$$

A- and C-horizon soils were air-dried, disaggregated if necessary, and sieved to <63 microns.

## **Analytical Techniques**

A large number of chemical elements were determined, using a variety of quantitative analytical techniques. XRAL Laboratories, Toronto, Canada, did all rock and A- and C-horizon analyses on contract to the USGS. O-horizon samples were analyzed in laboratories of the USGS in Denver, CO, following protocols described in Arbogast (1996). USGS analysts who provided laboratory assistance with organic samples are Paul Briggs, Zoe Brown, and Monique Adams. Analytical duplicate samples comprised about 10 percent of the total number of samples submitted. These duplicates are not retained in the accompanying data files. A description for each analytical technique and the laboratory where it was completed is given below.

### ***Inductively Coupled Plasma-Atomic Emission Spectroscopy***

Forty major, minor, and trace elements were determined in rocks and soil by inductively coupled plasma-atomic emission spectrometry. Each sample was decomposed using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids at low temperature. The digested sample was aspirated into the ICP-AES. Analyzed elements and lower detection limits are given in Table 1. USGS/XRAL

### ***Inductively Coupled Plasma-Mass Spectrometry***

Ashed O-horizon samples collected in 2000 were digested in a multi-acid mixture (hydrochloric, nitric, perchloric, and hydrofluoric acids) and analyzed for 42 major, minor and trace elements by ICP-MS. Analyzed elements and detection limits are given in Table 2. USGS

### ***Atomic Absorption Spectrophotometry***

Mercury was measured in rocks and soils using the cold-vapor AAS technique. Samples were decomposed in a mixture of nitric and hydrochloric acids. Potassium permanganate, sulfuric acid and potassium persulphate were added to the solution, followed by a NaCl-hydroxylamine solution and then transferred to a cold-vapor atomic

absorption mercury analyzer. The lower detection limit for mercury is 0.02 ppm. USGS/XRAL

For arsenic analyses, sample material was mixed with sodium peroxide and heated in a muffle furnace set at 750 °C for four minutes. The resulting sample mixture was cooled and diluted with 15 ml of water and 5 ml of concentrated hydrochloric acid. Ascorbic acid KI solution and hydrochloric acid were added to the mixture before being introduced to the AAS. The lower detection limit for arsenic is 0.6 ppm. USGS/XRAL

For selenium analyses, samples were mixed with nitric, hydrofluoric and perchloric acids and heated. After the solution cooled hydrochloric and nitric were added, and the mixture heated again and cooled prior to analysis by AAS. The lower detection limit for selenium is 0.2 ppm. USGS/XRAL

Two samples of rock collected from mine dumps and adits were analyzed for gold by AAS after collection by fire assay. The lower reporting limit for gold is 5 ppb. XRAL

#### ***Automated Carbon Analyzer***

A-horizon soil samples were analyzed for total carbon by combustion in an oxygen atmosphere at 1370°C to oxidize carbon to carbon dioxide. Moisture and dust were removed and a solid-state infrared carbon detector measured the carbon dioxide gas. The lower reporting limit is 0.05%. XRAL

#### ***Coulometric Titration***

A-horizon soils were analyzed for carbonate carbon by coulometric titration. The samples were treated with hot 2N perchloric acid and the evolved carbon dioxide passed into a cell containing a solution of monoethanolamine. The carbon dioxide, quantitatively absorbed by the monoethanolamine, was coulometrically titrated using platinum and silver/potassium-iodide electrodes. The lower reporting limit is 0.01%. XRAL

#### ***Automated Sulfur Analyzer***

Total sulfur was measured in A-horizon samples by mixing the soil with iron chips and LECOCEL. The mixture was heated in a combustion tube in a stream of oxygen at high temperature, oxidizing sulfur to sulfur dioxide, which was then measured by an infrared sulfur detector. The lower reporting limit for sulfur is 0.05%. XRAL

## **DESCRIPTION OF DATA FILES**

The analytical data files are provided as separate Microsoft Excel 2000.xls files. The samples are organized into media type with individual files for soils horizons and rocks samples. Five individual data files are included in this Open File. These are:

- 1) **Bedrock.xls** Bedrock geochemical data
- 2) **O\_2000.xls** Analyses of organic O-horizon samples collected in 2000. All elements except Hg have been converted from a measured ash-weight basis to a dry-weight basis. Hg values, which were determined from unashed sample, are not corrected for ash content.
- 3) **O\_2001.xls** Analyses of organic O-horizon samples collected in 2001. All elements except Hg have been converted from a measured ash-weight basis to a dry-weight basis. Hg values, which were determined from unashed sample, are not corrected for ash content.
- 4) **All\_A.xls** Analyses of A-horizon and E-horizon samples collected in both 2000 and 2001.
- 5) **All\_C.xls** Analyses of C-horizon soil samples collected in both 2000 and 2001.

## Common Data Fields

### *Field\_No.*

Field numbers for soils indicate the site label, the year of sampling, and the soil horizon. V-00-xx soil samples were collected in 2000, and V-01-xx soil samples were collected in 2001. VOYA- soil samples were collected in 2000 for a study on the impact of fire on soils. VR-x rock samples were collected in 2000. V-01- x rock samples were collected in 2001.

### *Coordinates*

Latitude and longitude for sample site locations are given in the data tables as decimal degrees. The coordinates were determined by GPS during sample collection. The datum was 1927 CONUS and the spheroid was Clarke 1866.

### *Geochemical Analyses*

All geochemical data are given in the following format. Field identifiers consist of three lines. The first line gives the chemical element symbol and unit of measurement. The second line is an abbreviated code for the analytical technique used for the element in that particular column. Reporting units are percent (%), parts per million (ppm), and parts per billion (ppb). The analytical methods codes are:

<b>ACA</b>	automated carbon analyzer
<b>ASA</b>	automated sulfur analyzer
<b>AAS</b>	atomic absorption spectrophotometry
<b>ICP_AES</b>	inductively coupled plasma-atomic emission spectroscopy
<b>CT</b>	colometric titration
<b>CV</b>	cold-vapor atomic absorption spectrophotometry for mercury
<b>ICP_MS</b>	inductively coupled plasma-mass spectrometry

For all geochemical data the symbol '<' indicates that an element was not detected at the lower limit of detection. A blank entry indicates that the samples were not analyzed for that particular element. The third line lists the laboratory (XRAL or USGS) where elemental analyses were done.

## Unique Data Fields

Individual data files have several unique fields.

### **Bedrock.xls**

*Rock\_Description* description of the rock type, based on field observations

### **O\_2000.xls and O\_2001.xls**

*Soil\_Horizon* Oi (forest litter) or Oe (forest duff)

*Horizon\_Thickness* estimated thickness of O-horizon

*ASH\_%* percent ash as calculated from formula given above

### **All\_A.xls**

*Soil\_Horizon* A- or E-horizon

*Horizon\_Thickness* estimated thickness of soil horizon

### **All\_C.xls**

*Depth* depth at which the sample was collected

## REFERENCES

- Arbogast, B.F., editor, 1996, Analytical methods manual for the Mineral Resource Surveys Program, U.S. Geological Survey: U.S. Geological Survey Open-File Report 96-525, 248 p.
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- Sado, E.V., Fullerton, D.S., Goebel, J.E., and, S.M., 1995, Quaternary geologic map of the Lake of the Woods 4° x 6° Quadrangle, United States and Canada: U.S. Geological Survey Miscellaneous Investigations Map I-1420 (NM-15), scale 1:1,000,000.



**Table 1. Lower detection limits for ICP-AES method (USGS and XRAL).**

<b>Element</b>	<b>Lower detection limit</b>
Aluminum, Al	0.005 %
Calcium, Ca	0.005 %
Iron, Fe	0.02 %
Potassium, K	0.01 %
Magnesium, Mg	0.005 %
Sodium, Na	0.005 %
Phosphorous, P	0.005 %
Titanium, Ti	0.005 %
Silver, Ag	2 ppm
Arsenic, As	10 ppm
Gold, Au	8 ppm
Barium, Ba	1 ppm
Beryllium, Be	1 ppm
Bismuth, Bi	10 ppm
Cadmium, Cd	2 ppm
Cerium, Ce	5 ppm
Cobalt, Co	2 ppm
Chromium, Cr	2 ppm
Copper, Cu	2 ppm
Europium, Eu	2 ppm
Gallium, Ga	4 ppm
Holmium, Ho	4 ppm
Lanthanum, La	2 ppm
Lithium, Li	2 ppm
Manganese, Mn	4 ppm
Molybdenum, Mo	2 ppm
Niobium, Nb	4 ppm
Neodymium, Nd	9 ppm
Nickel, Ni	3 ppm
Lead, Pb	4 ppm
Scandium, Sc	2 ppm
Tin, Sn	5 ppm
Strontium, Sr	2 ppm
Tantalum, Ta	40 ppm
Thorium, Th	6 ppm
Uranium, U	100 ppm
Vanadium, V	2 ppm
Yttrium, Y	2 ppm
Ytterbium, Yb	1 ppm
Zinc, Zn	2 ppm

**Table 2. Lower detection limits for samples analyzed by ICP-MS (USGS).**

<b>Element</b>	<b>Lower detection limit</b>
Aluminum, Al	0.005 %
Calcium, Ca	0.005 %
Iron, Fe	0.005 %
Potassium, K	0.005 %
Magnesium, Mg	0.005 %
Sodium, Na	0.005 %
Phosphorous, P	0.005 %
Titanium, Ti	0.005 %
Silver, Ag	0.5 ppm
Arsenic, As	1.0 ppm
Gold, Au	1.0 ppm
Barium, Ba	1.0 ppm
Beryllium, Be	0.1 ppm
Bismuth, Bi	1.0 ppm
Cadmium, Cd	0.1 ppm
Cerium, Ce	1.0 ppm
Cobalt, Co	1.0 ppm
Chromium, Cr	1.0 ppm
Copper, Cu	1.0 ppm
Europium, Eu	1.0 ppm
Gallium, Ga	1.0 ppm
Holmium, Ho	1.0 ppm
Lanthanum, La	1.0 ppm
Lithium, Li	1.0 ppm
Manganese, Mn	4.0 ppm
Molybdenum, Mo	0.5 ppm
Niobium, Nb	4.0 ppm
Neodymium, Nd	1.0 ppm
Nickel, Ni	2.0 ppm
Lead, Pb	1.0 ppm
Antimony, Sb	0.1 ppm
Scandium, Sc	2.0 ppm
Tin, Sn	1.0 ppm
Strontium, Sr	2.0 ppm
Tantalum, Ta	1.0 ppm
Thorium, Th	1.0 ppm
Thallium, Tl	1.0 ppm
Uranium, U	0.1 ppm
Vanadium, V	2.0 ppm
Yttrium, Y	1.0 ppm
Ytterbium, Yb	1.0 ppm
Zinc, Zn	2.0 ppm