

The Ontario Geological Survey Lake Sediment Geochemical Program: Progress Towards a Geochemical Map of Ontario, Canada

Introduction

A geochemical map of North America will likely be realized in the next few years with the completion of the Tri-National (Canada, USA and Mexico) soil geochemical landscapes project. On the eve of this project, it is fitting to reflect on the geochemical mapping efforts within the province of Ontario in central Canada (Fig. 1) and in particular the contribution of an early and ardent supporter

of landscape geochemical mapping, the late John Fortescue. John proposed the concept of a geochemical map of Ontario almost 25 years ago (Fortescue 1983). In the decade that followed, the only progress made at the Ontario Geological Survey (OGS) to specifically address this concept were several demonstration or “pilot” projects that involved either grid (module) sampling (e.g. stream sediments in southern Ontario; Fortescue 1984, 1992) or province-wide geochemical traverses (lake sediment and water; Fortescue & Dyer 1993, 1994a,b). These were “low density” geochemical sampling projects over diverse landscapes of Ontario, aimed at testing the ability to delineate province-wide geochemical patterns of pertinence to mineral exploration and environmental geochemistry. However, Fortescue was also instrumental in initiating the high density (approximately 1 sample per 3 km²) lake sediment geochemical program at the OGS, which is now in its 20th year. This program takes advantage of the greater than 250,000 lakes covering almost 1/5th of Ontario’s 1,000,000 km² surface area. The program mandate has always been twofold: 1) to support mineral exploration by sampling in areas of high mineral potential; and 2) provide high quality baseline geochemical data of the province.

Across the province, over 60,000 samples have now been collected covering an area of more than 200,000 km² (Fig. 1). Ironically, there are now so many contiguously sampled areas (Fig. 1) that the result is approaching Fortescue’s vision of a province-wide geochemical map, at a much higher density than he might ever have hoped.

The OGS lake sediment and water dataset is so large and high-density that displaying significant portions of the data using conventional geographic information systems (GIS) is sometimes very slow – even with fast computers. To address this problem, the OGS has developed “OGS-Earth” as an, as yet, in-house add-on to Google-Earth for the purpose of rapid integration of multiple geological data layers, including the lake geochemical datasets. The platform allows the visualization of geological, topographic and cultural information with overlain geochemistry

in virtual 3-D through all scales and view angles. Even to novice users, profound geochemical trends and relationships between geochemistry and geology can be immediately apparent – and the platform is considerably easier to operate than a typical GIS.

Sampling methods

From the outset of the high density lake sampling program in 1987, the application of a robust and consistent sampling protocol was considered paramount and this is still the case. Lake sediment and water sampling is performed by 2-person teams primarily from float-equipped Bell 206B helicopters. During the mid-1980s, Fortescue developed a gravity coring device that allowed for the rapid collection of lake sediments and the reliable discrimination between surface and deep lake sediment (Fortescue 1988). The sampler and associated equipment

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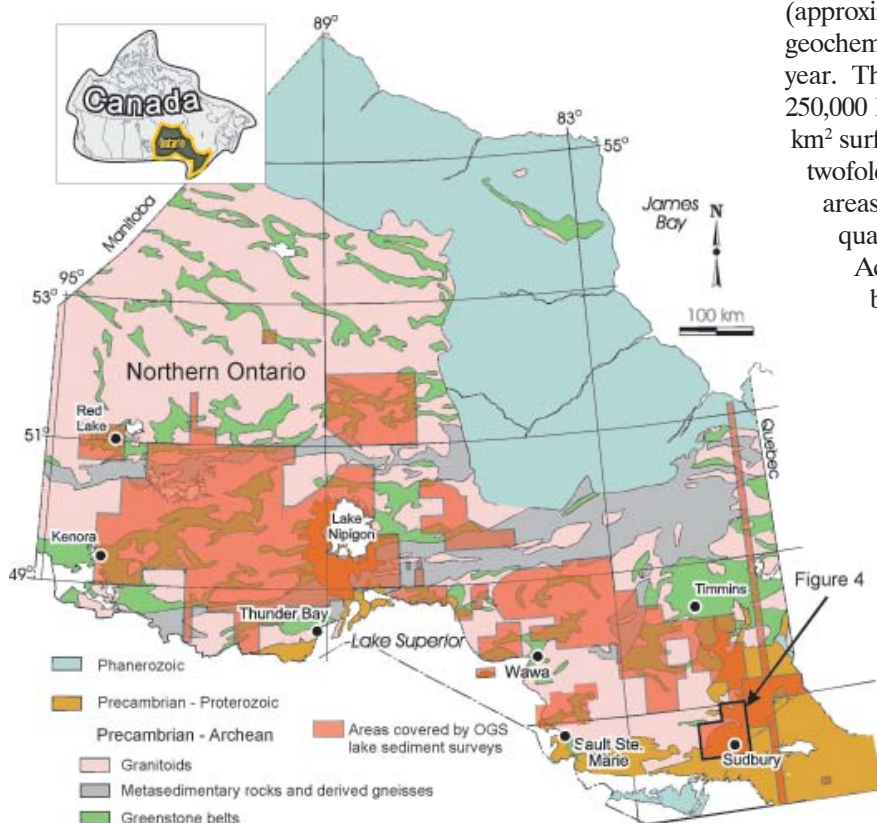


Figure 1. High density lake sediment coverage of northern Ontario.

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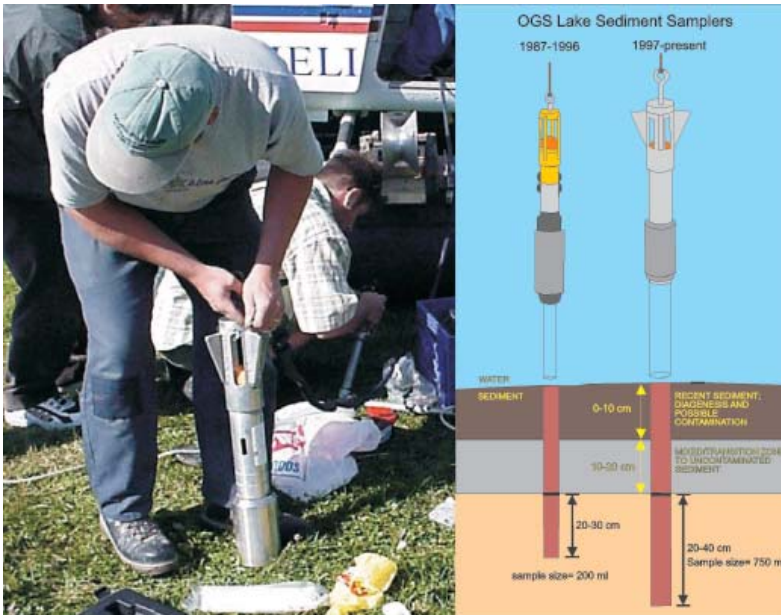


Figure 2. Ontario Geological Survey lake sediment gravity core sampler.

have been improved and refined over the past 20 years (Fig. 2), but the basic concept has remained the same. Intact lake cores are retrieved from the lake bottom in a polycarbonate tube. Bottom-up extrusion of the sediment allows for discrimination between shallow (0-15 cm)

sediment and deeper sediment (e.g. >20 cm) (Fig. 2). All samples are taken from depths >20 cm below the sediment–water interface (SWI) in order to avoid anthropogenic influences and near surface diagenetic effects. Therefore, these deeper sediments more accurately reflect the natural geochemical inputs, which may be traced back to local bedrock geology. If required, the upper (shallow) sediment can also be kept as a separate sample to characterize potential anthropogenic inputs, for example, near industrial areas or existing mines.

Lake water samples are taken simultaneously with the sediment samples using a semi-automated water sampling apparatus, consisting of a pump, a multi-parameter water quality analyzer (for measurement of parameters such as pH, temperature and conductivity), and a variety of hoses and valves. Lake water is pumped through the system in order to purge it prior to the collection of a sample and for the measurement of water quality data. The water samples were kept cool immediately following collection and are processed (filtered/acidified), within 12 hours of collection.

Accurate sample site locations and flight tracks are recorded by GPS receiver. A new innovation in 2006 was the introduction of a GPS receiver mated to a tablet computer to provide “heads up” real-time navigation between lake sites, which in recent years had been the rate determining part of the methodology. Average sampling

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production is approximately 20-24 samples per flight hour.

The use of deep lake sediment

In order to avoid anthropogenic influences due to water and airborne contaminants, the sampling of deep lake sediment has always been considered an essential part of the OGS lake sediment sampling program. The practise of consistently sampling the deep (>20 cm) lake sediment was initially based on studies by Dickman & Fortescue (1984, 1991) and Fortescue et al. (1984) on the rise of *Ambrosia* pollen at a sediment depth of 10 to 15 cm within 8 test lakes in the Sudbury and Wawa regions. This rise in the ragweed pollen *Ambrosia* corresponds to the onset of extensive deforestation associated with agricultural development during the post-industrial period of the past 100 years. The age of the *Ambrosia* pollen rise has been verified by ^{210}Pb dating of lake sediment cores, including two lakes north of Lake Wanapitei (Dickman & Fortescue 1991). At these lakes the pollen rise occurred between 14 and 17 cm depth with a calculated sedimentation rate of approximately 1.2 mm per year.

The standardization to a deeper 20 cm depth was done to account for variations in sedimentation rates between different landscape environments. Data from a recent study in the Sudbury area confirm that a sample depth of >20 cm is adequate to avoid contamination (Hunt 2003). Hunt's study involved Pb^{210} age dating of lake sediment cores obtained with a KB gravity corer from 14 lakes. The sedimentation rate averaged 1.6 cm per decade, therefore a 20 cm depth in lake sediment corresponds to approximately 125 years ago. Eleven of the lakes cored by Hunt (2003) were sampled by the OGS with the coring torpedo shown in Figure 2. The geochemical results are very similar indicating that the OGS sampling methodology is successful at obtaining and discriminating between recent and pre-industrial sedimentation.

Sample Preparation, Analytical Methods and Quality Control

Sediment samples are partially air dried in the field prior to delivery to the OGS Geoscience Laboratory (GeoLabs) in Sudbury. Final drying is carried out at <40° C followed by disaggregation with a ceramic ring and puck pulverizer for approximately 20 seconds. Samples are sieved to obtain a -60 mesh (<250 μm) size fraction for analysis. Analysis at the OGS laboratory consists of aqua regia digestion of 0.5 g of sample pulp followed by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) for the determination of approximately 50 trace, minor and major elements. Loss-on-ignition (LOI) is determined at 500° C under an oxygen atmosphere using an automated gravimetric technique. Approximately 10 g of each sample pulp are pressed into briquettes prior to instrumental neutron activation analysis (INAA) to determine Au, As and 24 other elements. Water samples are passed through 0.45 μm syringe filters and acidified to 1% with ultrapure nitric acid within 12 hours of sample collection. The analysis of water is by direct aspiration ICP-MS at the OGS laboratory to determine approximately 50 elements.

Quality control is monitored through sample pulp replicates, field duplicates, CANMET certified reference materials and internal (OGS collected) bulk standards. Quality control (QC) samples are inserted into the sample sequence at the rate of 1 QC sample per 10 unknowns. Analytical precision for each element is determined by plotting duplicates data on an X-Y chart and determining the variation of 95% of the data from a 1:1 ratio. Accuracy is determined by plotting the sequential values returned for certified reference standards inserted in the batch against a vertical scale of concentration and comparing this with the "provisional values" (Lynch 1990) for the standards.

The controls on natural baseline lake geochemistry: An application of 'OGS-Earth'

The integration of OGS geoscience data into Google-Earth through the OGS-Earth application has important advantages. In our experience, it is superior to conventional GIS in several ways:

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1. It is much faster for display, panning, zooming and rotation of large amounts of data.
2. Radio buttons and dimmer-bars allow an instantaneous visual assessment of the relationship between underlying layers of data, and are faster and easier to use than similar features in GIS applications.
3. Angled, oblique and DEM-based 3 dimensional views are possible, which helps to outline linear trends in data and topographic effects.
4. Since both cultural and geological data can be displayed simultaneously with geochemical data, OGS-Earth is particularly well suited for distinguishing the source of geochemical signals as geological or anthropogenic.
5. Google-Earth is optimized for web-browsers and is therefore potentially an excellent tool for the display of published OGS data on the internet.
6. The basic Google-Earth software is free and very easy to use, and therefore, in conjunction with OGS-Earth, it is likely to be more useable for a much wider audience than conventional GIS.

Figure 3 is an example of lake sediment data for northwestern Ontario, displayed using OGS-Earth. Calcium concentration in lake sediments varies widely across a total area of over 100,000 km² and broad regional trends related to geology are immediately obvious. Much higher concentrations of Ca occur in sediments north of Lake Nipigon, derived from local till which has been transported southwest by glaciers from the sedimentary carbonate rocks of the James Bay Lowland. The mafic rocks around Lake Nipigon (pale orange, Fig. 3b) are the source material for Ca in lake sediments to the southwest of the lake. Local trends are also obvious across a wide range of scales. In the Atikokan area, the greenstone belts (Fig. 3c; northeast and east-west trending green units) show significantly elevated Ca concentrations in sediments over the greenstone and immediately down-ice relative to those that occur over the surrounding plutonic rocks. Trace elements can also show excellent lithological associations in addition to being indicative of localized mineralization. For example, Cu is generally elevated over mafic rocks and Ni over ultramafic rocks but much higher concentrations are noted near sulphide mineralization known to host Cu and Ni ore minerals.

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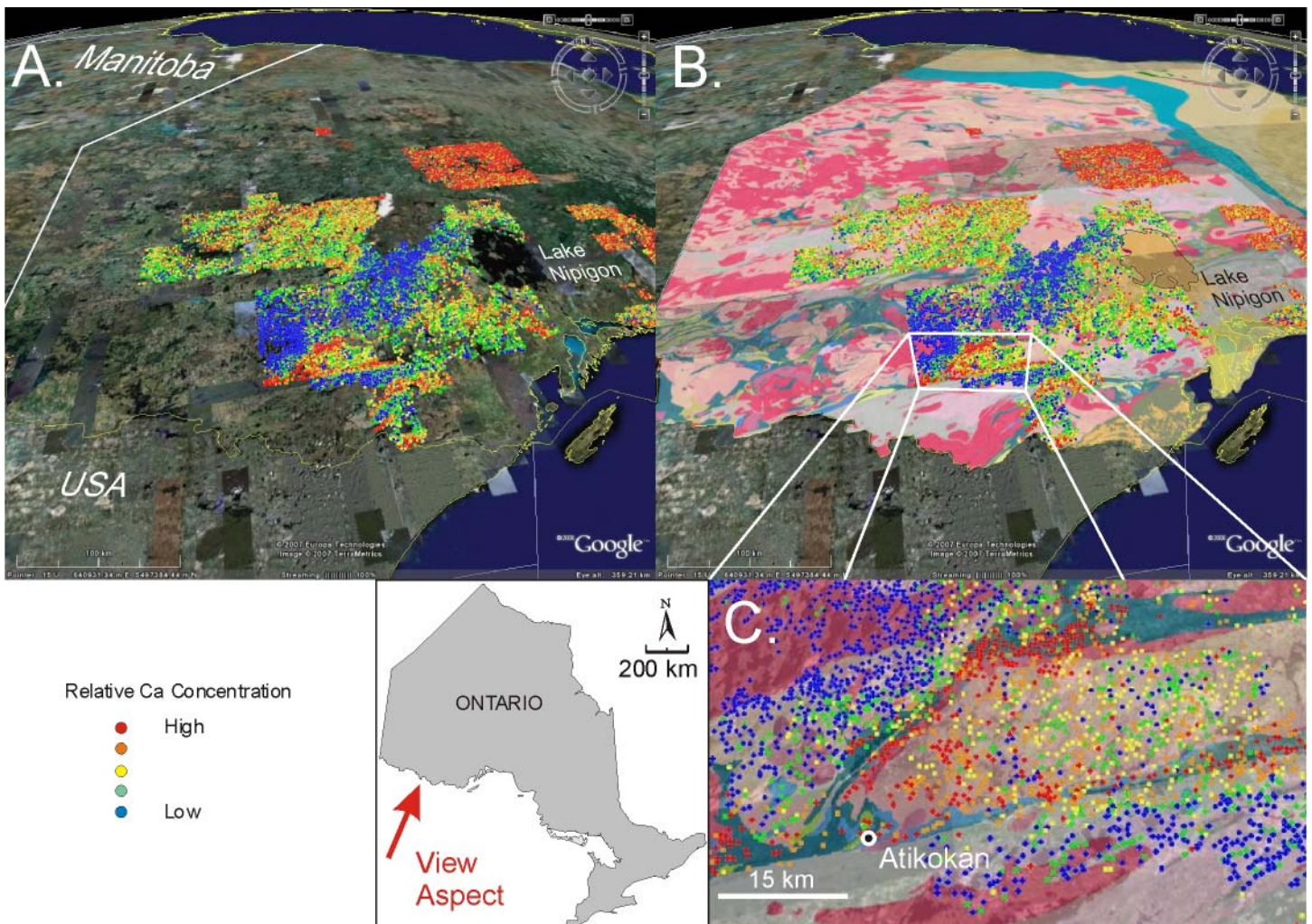


Figure 3. Calcium in lake sediments in northwestern Ontario, displayed in Google-Earth® and plotted using the 'OGS-Earth' application. Fig. 3A shows sample locations colour-coded by concentration on the Google-Earth® satellite-image fabric. Fig. 3B shows the same sample locations overlain on OGS bedrock geology. Fig. 3C shows a blow-up of the Atikokan area with volcanic rocks shown in green.

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The ease with which geochemical data can be visualized in Google Earth has important implications to geochemistry beyond the display of OGS data. This platform is not hindered by the size of the geochemical dataset and it can reach a worldwide audience. As such, Google Earth could be the platform for the integration of other provincial or continental scale geochemical mapping efforts, ultimately leading to a geochemical map of the Earth.

Distinguishing natural geochemical baseline from anthropogenic lake sediment signal in the Sudbury Mining District

Environmental disturbance in the Sudbury area

A significant mining and smelting “footprint” exists in the Sudbury basin which hosts numerous world-class Ni-Cu-PGE deposits. This footprint poses a challenge for the use of lake sediment geochemistry in the region. Whether the objective is baseline geochemical mapping or mineral exploration, it is difficult to “see” through the ecological disturbance to understand background geochemical conditions as they would have existed prior to industrial activity. Environmental impact in Sudbury and the surrounding area is the result of many factors that occurred throughout the century prior to the 1980s, when both remediation and major reductions in emissions took

place. These factors include mining (sulfur dioxide fumigation and metal deposition), intense logging, bush fires, water and wind erosion and enhanced frost action (Winterhalder 1995). In particular, the roast yards that operated on the south range of the Sudbury basin from 1888-1929 created sulfuric acid fogs that suffocated and burnt vegetation and acidified the surrounding soils, lakes, streams and rivers. The smelter emissions over the years caused what is commonly referred to as the Sudbury “footprint”, visible on satellite images, which resulted from the loss of vegetation in the vicinity of the smelters. The areal extent of vegetation damage in the Sudbury area, determined in the early 1970s, covered a surface area of approximately 720 km². Not so obvious is that lakes as far as 100 km to the northeast had also been affected (Neary et al. 1990).

Water quality monitoring in the 1970s revealed that 7000 lakes within a 17000 km² area have been measurably affected by the Sudbury emissions (Dixit et al. 1995). This disturbance is manifest as acidified lakes, metal-contaminated lake sediments, and indirect effects resulting from damage to vegetation in the lake basins. It is likely that these effects have been amplified due to the fact that Sudbury is situated on the Precambrian Shield. The rock offers very little buffering capacity and therefore local soils are sensitive to acidification. The minor amounts of calcareous rock and low carbonate drift materials over Precambrian shield rocks in the area cannot neutralize the acidity formed in the byproducts of Sudbury’s mining industry (Bajc & Hall 2000).

The lake sediment geochemical response in the Sudbury area

The distribution of Ni in lake sediment for the Sudbury area is displayed in Figure 4(b) (Dyer et al. 2004). For comparison, data from the Geological Survey of Canada’s National Geochemical Reconnaissance (NGR) program (Hornbrook & Friske 1988; Friske et al. 1997) are presented in Figure 4(a). The NGR sampling was carried out during the 1970s and 80s at a much lower density (approximately 1 sample per 13 km²) than the current OGS program and using a different type of gravity sampler known as the Hornbrook sampler (Friske 1991). This device was not designed to discriminate between shallow and deep sediment, but rather, to obtain a very fast ‘grab’ sample of lake sediments. Because of its

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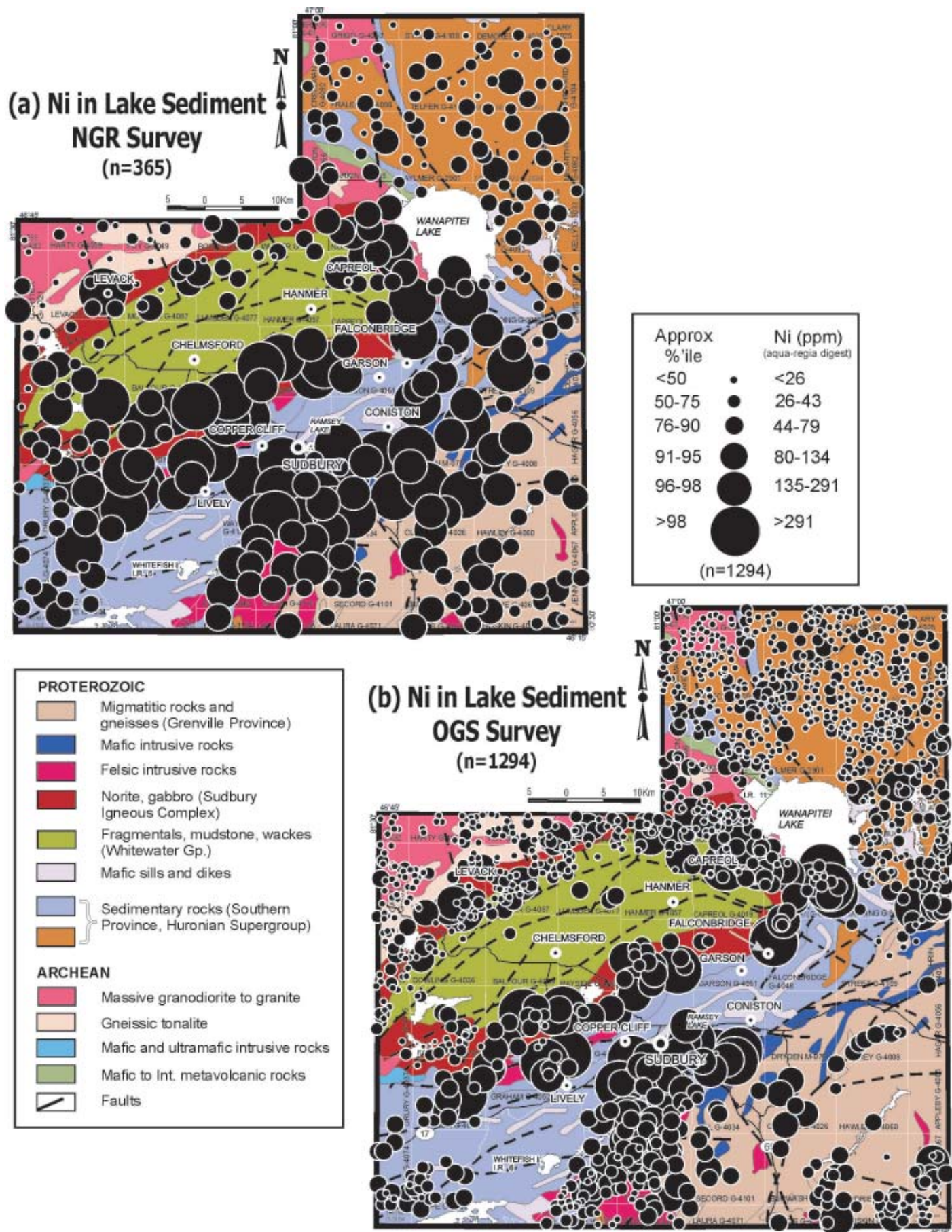


Figure 4. Nickel concentrations in the greater Sudbury area lake sediments.

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design, the entire 72 cm sampler must completely penetrate the bottom mud in order to be sure that the material retrieved is from a depth greater than 20 cm. Additionally, a butterfly valve in the nose of the sampler serves to disturb the sediment during penetration of the lake bottom. Therefore, this sampler obtains lake sediment from variable depth below the sediment water interface, depending on its depth of penetration into the lake sediment. The sample preparation and analysis of samples from both surveys were similar including the use of an aqua regia digest. Quality control for both NGR and OGS surveys was monitored through replicate analysis of unknowns and the insertion of CANMET certified reference materials (e.g. LKSD-1, LKSD-4).

Figure 4 (a) and (b) reveals that for most lakes, Ni concentrations obtained by the OGS survey are considerably lower than in the NGR data. Results for lakes that were sampled by both surveys (n=193) were compared because the differences in methodology of the two surveys provides insight into the sources of metals in sediments in this area (Fig. 5). To ensure consistent sample media from the two surveys and methodologies, the results for each lake that was sampled by both methods were examined closely to ensure a similar lake depth and LOI level. Any sample sites with a significant discrepancy were screened out of the comparison dataset and a visual check was done in ArcMap GIS to ensure sample sites from each survey were located within the same lake basin. Despite the differences in sample density, it is clear that many of the NGR samples contained significantly higher levels of Ni than the OGS samples.

Most of the regional distribution of Ni portrayed in Figure 4(b) is spatially associated with Sudbury Igneous Complex (SIC) rocks, which host most of the Ni mineralization in the Sudbury basin. Anomalies due to contamination are localized to lakes in close proximity to tailings/slag/waste rock, or lakes in which the natural sediment record has been compromised, possibly by higher sedimentation rates (resulting in more than 20 cm of young sediments) due to enhanced erosion of Sudbury area soils as a result of de-vegetation due to fumigation from roasting/smelting operations in the early 1900's. A

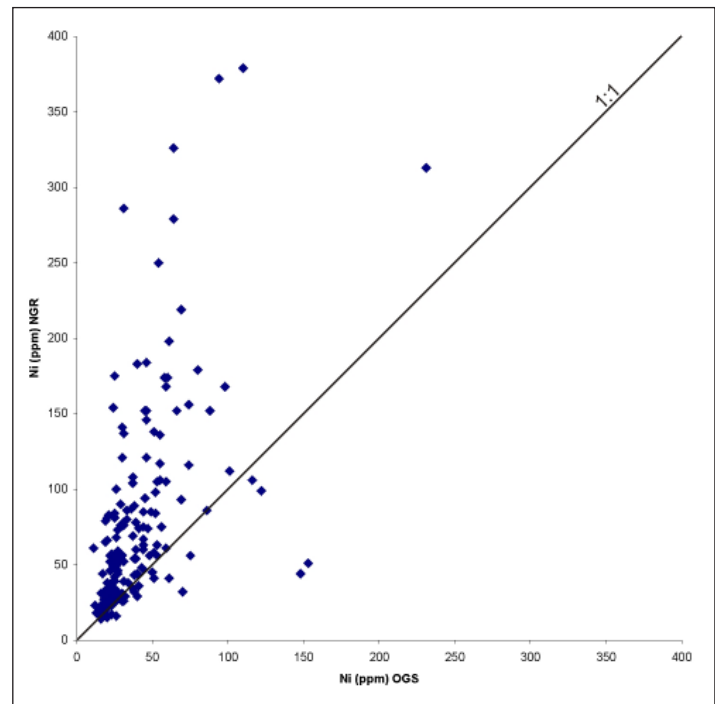


Figure 5. Plot of Ni concentrations obtained from the same lakes by the National Geochemical Reconnaissance program and by the Ontario Geological Survey regional survey.

pattern of elevated Ni concentrations occurs in some urban Sudbury lakes south of Ramsey Lake, Coniston and Copper Cliff. The elevated Ni which extends further to the south may be in response to the presence of the Ni-

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mineralized Copper Cliff offset dike and Nipissing gabbro rocks, as well as erosion and glacial dispersion southward from the Sudbury Igneous Complex.

The pattern differences between the two datasets suggests the OGS protocol of sampling a discreet depth interval of deeper sediments is successful in obtaining relatively undisturbed and uncontaminated sediments in the vast majority of cases. The results also demonstrate that natural concentrations of metals in the surficial landscape can exceed regulatory limits. For example, a total of 134 lake sediment samples from the OGS survey have natural Ni concentrations that exceeded the severe effect level of 75 ppm, as set by the Provincial Sediment Quality Guidelines for Ontario.

Summary

The OGS lake geochemical sampling program was designed to obtain a high density, high quality natural geochemical signal in areas of high mineral exploration potential. It is intended both as a record of natural baseline conditions in pre-industrial sediments and a mineral exploration tool. An excellent example of this is the high

density survey over the Sudbury region, where, despite the significant mining activity and significant ecological disturbance, the OGS lake sediment sampling methodology was successful in obtaining relatively undisturbed and uncontaminated deep sediments in the vast majority of cases. Recent development of 'OGS-Earth', a prototype add-on to Google Earth has allowed very fast and easy visual display of the entire dataset at any scale and viewing angle. In future, it may be utilized to allow web access to the OGS lake geochemical dataset. Currently, all OGS lake sediment digital datasets and Open File Reports (OFR) are available for free download from the Ontario Ministry of Northern Development and Mines, Geology Ontario website (www.geologyontario.ca). Although the high-density lake sediment program was never intended as such, its coverage has increased in recent years to such an extent that it represents a quasi-provincial scale geochemical map of lake sediments, thus realizing one of the late John Fortescue's career-long goals. Other initiatives currently underway in Ontario and beyond will also likely realize this goal including the Tri-National Soil Survey and the Provincial Groundwater Geochemical Characterization study.

Acknowledgements

The authors wish to thank Jiro Shirota for his expertise with regard to Google Earth and the development of OGS-Earth. Timely assistance with figure generation for this manuscript is extended to Vanessa Felix. The manuscript benefited greatly from a review by Cam Baker and is

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Richard Dyer

Email: richard.dyer@ontario.ca telephone: 705-670-5916

Stewart Hamilton

Email: stew.hamilton@ontario.ca telephone: 705-670-5915

*Sedimentary and Environmental Geoscience Section,
Ontario Geological Survey,
933 Ramsey Lake Road,
Sudbury, Ontario,
CANADA P3E 6B5*

