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Article abstract

Loons in Kejimkujik National Park, located in southwestern Nova Scotia, contain the highest mercury concentrations in blood of any breeding loon population tested in North America. A team of multi-disciplinary scientists has completed extensive research within and around the park in an attempt to identify the source(s) and process(es) that may be responsible for the high levels of mercury. One aspect of the research involved the collection of 32 C-horizon till samples from depths ranging from 70 to 120 cm. The samples were collected at 100 to 200 m intervals from three northwest-southeast transects that cross the inferred contact between the Halifax and Goldenville formations south of the Kejimkujik National Park boundary. Geochemical analysis (<63 µm size fraction) of the till indicates that the mean Hg concentrations are 40.8 ppb for till overlying slate of the Halifax Formation, and 32.4 ppb for till overlying greywacke of the Goldenville Formation. Chemical analyses of 9 bedrock samples (<105 µm size fraction) returned very low Hg concentrations (mean 2.4 ppb). Strict quality assurance/quality control protocols were followed in the collection, preparation, and analysis of the till and bedrock samples.

Mercury in till and bedrock southeast of Kejimkujik National Park, Nova Scotia

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ABSTRACT

Loons in Kejimkujik National Park, located in southwestern Nova Scotia, contain the highest mercury concentrations in blood of any breeding loon population tested in North America. A team of multi-disciplinary scientists has completed extensive research within and around the park in an attempt to identify the source(s) and process(es) that may be responsible for the high levels of mercury. One aspect of the research involved the collection of 32 C-horizon till samples from depths ranging from 70 to 120 cm. The samples were collected at 100 to 200 m intervals from three northwest-southeast transects that cross the inferred contact between the Halifax and Goldenville formations south of the Kejimkujik National Park boundary. Geochemical analysis (<63 µm size fraction) of the till indicates that the mean Hg concentrations are 40.8 ppb for till overlying slate of the Halifax Formation, and 32.4 ppb for till overlying greywacke of the Goldenville Formation. Chemical analyses of 9 bedrock samples (<105 µm size fraction) returned very low Hg concentrations (mean 2.4 ppb). Strict quality assurance/quality control protocols were followed in the collection, preparation, and analysis of the till and bedrock samples.

RÉSUMÉ

Les huards du parc national Kejimkujik, situé dans le Sud de la Nouvelle-Écosse, présentent les concentrations de mercure dans le sang les plus élevées parmi toutes les populations de huards examinées en Amérique du Nord. Une équipe pluridisciplinaire de scientifiques a réalisé des travaux de recherche approfondis à l'intérieur et à proximité du parc pour tenter de repérer la ou les sources et le ou les processus à l'origine des concentrations élevées de mercure. Un volet de ces recherches a comporté le prélèvement de 32 échantillons de till de l'horizon C à des profondeurs variant entre 70 et 120 cm. Les échantillons ont été prélevés à des intervalles de 100 à 200 m à l'intérieur de trois transects du nord-ouest au sud-est traversant la présumée zone de contact entre les formations d'Halifax et de Goldenville, au sud de la limite du parc national Kejimkujik. Une analyse géochimique (fraction d'une dimension de moins de 63 µm) du till révèle des concentrations moyennes de Hg de 40,8 p.p. 10^9 b dans le till recouvrant l'ardoise de la Formation d'Halifax et de 32,4 p.p. 10^9 dans le till recouvrant la grauwacke de la Formation de Goldenville. Des analyses chimiques de neuf échantillons de substrat rocheux (fraction d'une dimension de moins de 105 µm) ont accusé des concentrations très faibles de Hg (en moyenne 2,4 p.p. 10^9). Les chercheurs ont suivi des protocoles rigoureux d'assurance/de contrôle de la qualité lors du prélèvement, de la préparation et de l'analyse des échantillons de till et de roche du substratum.

[Traduit par la rédaction]

INTRODUCTION

Loons in Kejimkujik National Park (KNP), southwestern Nova Scotia, have the highest mercury (Hg) concentration in blood of any breeding loon population in North America (Burgess *et al.* 1998, 2005; Burgess and Hobson 2006). For the past several years, a multi-disciplinary team of research scientists has been attempting to identify the potential Hg source(s) and process(es) responsible for the anomalous Hg levels. A geochemical component of this research involved the collection and chemical analysis of till and bedrock samples to quantify the geogenic contribution of naturally occurring Hg concentrations from glacial sediments overlying bedrock sources within the Meguma Group, in particular the Goldenville Formation – Halifax Formation Transition Zone (GHTZ).

The study, located on N.T.S. map sheet 21A/06, just south of the Kejimkujik National Park boundary, was divided into three components: 1) bedrock and surficial mapping of the various stratigraphic units, 2) till and bedrock geochemical sampling/analysis, and 3) a detailed ground magnetic survey

to accurately locate the contact between the Goldenville and Halifax formations.

BEDROCK GEOLOGY

The study area is located just south of Kejimkujik National Park and is underlain by rocks of the Meguma Group (Fig. 1). Outcrop exposure is rare (<2%) and found mainly along roadside ditches and watercourses. The oldest rocks consist of massive grey to green greywacke and minor laminated grey to black metasiltstone of the Goldenville Formation. These are overlain by finely laminated greenish grey to black slate and metasiltstone of the Halifax Formation (Williams *et al.* 1985; Horne and Corey 1994).

The contact between the coarse-grained Goldenville Formation and fine-grained Halifax Formation is gradational and referred to as the Goldenville - Halifax Transition Zone. The GHTZ is known for its distinctive rock types characterized by a Mn-rich, spessartine garnet-bearing, coticule horizon interstratified with slate and greywacke (Graves and Zentilli 1988). The GHTZ is characterized geochemically by the presence of anomalous concentrations of metals including Mn, Ba, Pb, Zn, Cu, Mo, W, and Au (Graves and Zentilli 1988). The GHTZ is further characterized by layers rich in pyrite and pyrrhotite that may play an important role in Hg cycling when sulphide mineral oxidation allows the release of metals in the environment (Fox *et al.* 1997). The contact between the Halifax and Goldenville formations is not exposed in the study area. Devonian monzogranite, namely the Scrag Lake and Kejimkujik plutons, and leucomonzogranite, the Davis

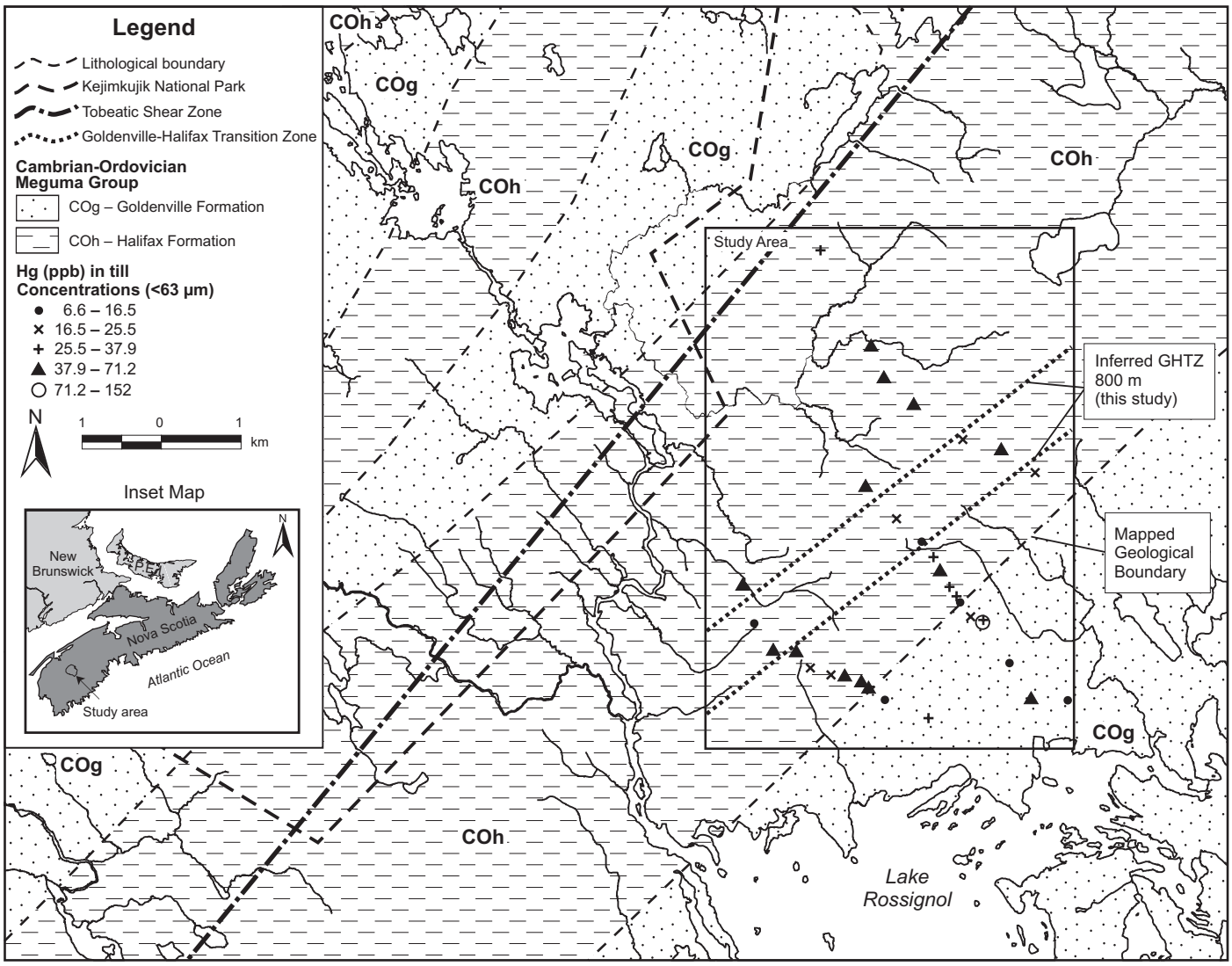

Fig. 1 Bedrock geology of the study area and part of Kejimkujik National Park, showing the location of the inferred Goldenville – Halifax Transition Zone (GHTZ) and the position of the actual mapped contact. Till sample locations with Hg concentrations (ppb) are shown along the three transects. Geology after Horne & Corey (1994).

Lake Pluton, intruded the Halifax and Goldenville formations (Horne and Corey 1994).

SURFICIAL GEOLOGY

The surficial geology of the study area is characterized by the Late to Middle Wisconsinan Beaver River Till (Finck *et al.* 1994). Two facies of the Beaver River Till are present in the study area, the clay-rich slate facies derived from slate of the Halifax Formation and the sandy greywacke facies derived from metasedimentary rocks of the Goldenville Formation. The major glacial transport direction for the Beaver River Till is southeastward over the South Mountain Batholith with a short dispersal distance (< 1 km), resulting in a locally derived till varying in thickness from 1 to 6 m. During the field mapping and sampling program, ice-flow indicators such as glacial striations were identified and recorded confirming the regional transport direction of Stea (1982).

PREVIOUS WORK

Smith (2000) reported that the average Hg concentration in bedrock in southwestern Nova Scotia is 3.3 ppb (n = 146). The mean Hg content in greywacke of the Goldenville Formation is lowest (1.0 ppb), closely followed by granite (1.5 ppb), and slate of the Halifax Formation (2.5 ppb). The highest Hg concentrations are in the biotite separates from monzogranite (13.8 ppb) and Silurian rocks (diabase dykes, sills, and associated siltstone) from the Bear River area (12.2 ppb). Page and Murphy (2003) postulated that biotite in granite may be a significant contributor to distribution and migration of Hg in southwestern Nova Scotia. In another study, unweighted averages for various rock types in Kejimkujik National Park indicate that the average Hg concentration is in the order of 4.4 ppb (Smith *et al.* 2005).

Sangster *et al.* (2001) summarized the Hg concentrations in different lithologies throughout Kejimkujik National Park, including data from drill core from the eastern part of the Meguma Terrane. They observed that the lowest Hg concentrations are in the Goldenville Formation (<0.5 ppb to 4.0 ppb; n = 47) and in monzogranite of the Kejimkujik Pluton (<0.5 ppb to 5.8 ppb; n = 31). They also observed that the Halifax Formation had slightly higher Hg concentrations, ranging from <0.5 ppb to 16.4 ppb (n = 100). Sangster *et al.* (2001) concluded that Hg could be transferred during the earliest weathering stages and is most pronounced in the porous, well-cleaved, sulphidic black slate that contains 5% pyrite and/or pyrrhotite. The higher concentrations of Hg observed in drill core samples suggest that surface bedrock sampling may not accurately account for all the Hg present in the bedrock, as significant amounts may have been leached during secondary weathering processes (Sangster *et al.* 2001). Goodwin (2005) reported the results of Hg concentrations for ninety-seven till samples collected mostly from within Kejimkujik National Park.

METHODOLOGY

During the summer of 2001, a geochemical, geological, and geophysical field program was completed in the study area. This involved (1) till and bedrock sampling, (2) geological mapping and (3) approximately 11 km of detailed total field ground magnetic surveying. Three NW–SE transects ranging from 2.3 km to 3.7 km in length that crossed the inferred Halifax Formation – Goldenville Formation contact were used for control of this contact zone (Fig. 1).

A total of 32 C horizon till samples were collected at 100 to 200 m intervals from the same three NW–SE transects used for the detailed total field ground magnetic survey. Samples were collected by shovel at depths ranging from 70 to 120 cm, which is beyond the depth of anthropogenic atmospheric influence (Henderson and McMartin 1995). Till clast identification and counts were completed on 11 samples collected from transects two and three. Nine rock samples were collected from exposed slate and greywacke outcrops along the same transects.

Sieved till (<63 microns) and crushed rock samples (<105 microns) were digested in *aqua regia* and analyzed for Hg by CETAC Cold Vapour Atomic Absorption (34 additional elements) with a lower detection limit of 1 ppb, by ACME Analytical Laboratories Ltd., Vancouver, B.C. Particular attention was given to quality control protocols during the entire program. This control included the insertion of certified standards, preparation splits and field duplicates (representing about 15% of the samples submitted for analysis) during the collection, preparation, and analysis of the till and rock samples.

Total field magnetic readings were acquired at 12.5 m spacing along each of the three traverses crossing the inferred Halifax Formation – Goldenville Formation contact (Fig.1). All readings were subsequently corrected for diurnal drift.

RESULTS AND DISCUSSION

Till geochemistry

The highest reported Hg concentration from the 32 till samples was in till derived from the Halifax Formation slate. Mercury concentrations ranged from a low of 13.2 ppb to a high of 151.5 ppb (n = 20; mean 40.8 ppb; σ = 31.12; Fig. 2a). Till derived from the Goldenville Formation metasandstone contains Hg concentrations ranging from 6.6 ppb to 71.2 ppb (n = 12; mean 32.4 ppb; σ = 19.21; Fig. 2b). Till sample locations with associated proportional symbol plots for Hg concentrations are presented in Fig. 1. Mean Hg in till concentrations from this study are slightly lower than mean Hg content for till

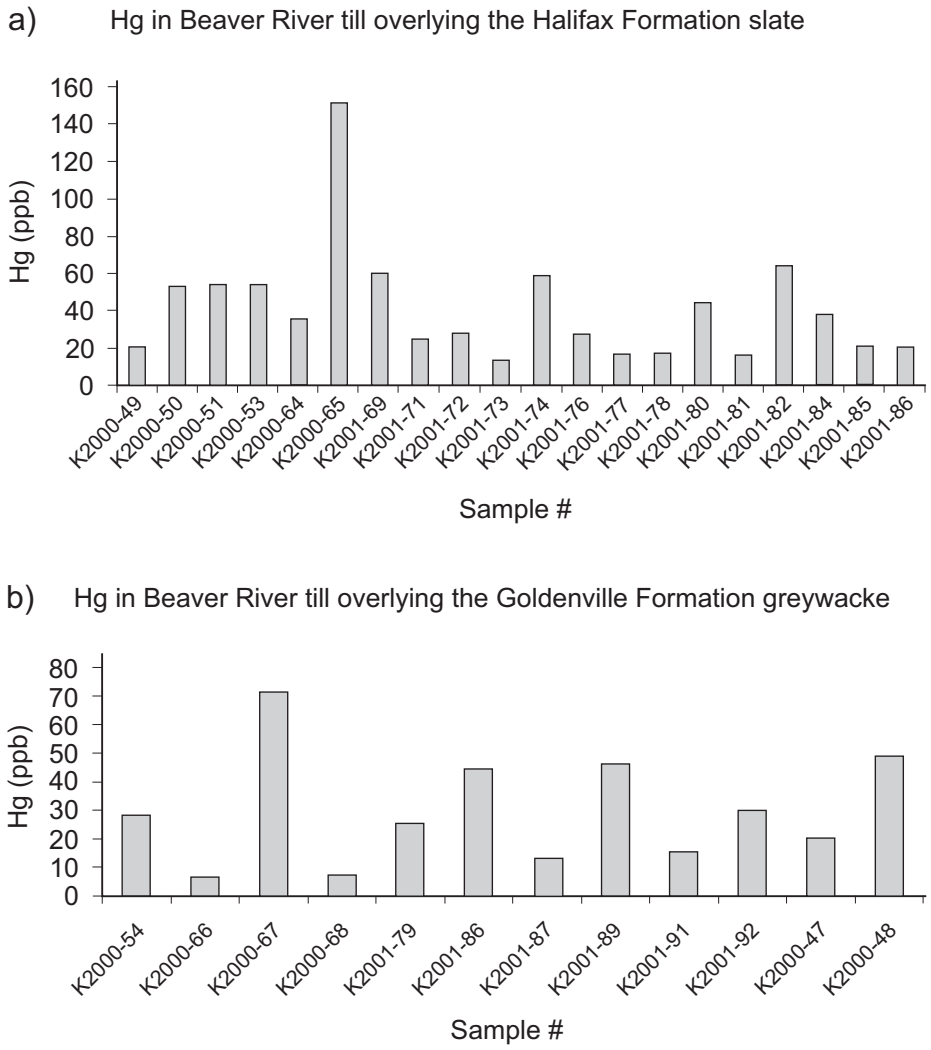

Fig. 2 Mercury concentrations in (a) the clay-rich slate facies of the Beaver River till and (b) the sandy greywacke facies of the Beaver River till.

(50 ppb) reported by Jonasson and Boyle (1972). Complete geochemical and geo-referenced data for the study area are available in tabular format in Culgin (2002).

Clast identification and counts

The clast identification and counts from the >4 mm pebble fraction of eleven till samples confirm the presence in the study area of two facies of the Beaver River Till (Finck *et al.* 1994), a clay-rich slate facies and a sandy greywacke facies (Fig. 3). The generally southeast ice-flow direction was also confirmed and a dispersal distance of approximately 900 m was determined on the basis of the percentage (>50%) of greywacke clasts down-ice from the contact of the Halifax/Goldenville formations. The contact was interpreted from the total field magnetic survey. The x-y plot (Fig. 3) of the relative proportion of Halifax Formation slate clasts recovered from till samples indicates that the relative width of the Halifax Formation slate subcropping in the study area may be significantly less than shown on the most recent published geology map (Horne and Corey 1994).

Rock geochemistry

A total of nine bedrock samples were collected and subsequently analyzed for Hg during this study. All rock samples returned low Hg concentrations ranging from 0.2 ppb to 3.4 ppb (mean 2.4 ppb; n= 9; $\sigma = 0.91$; Fig. 4) including two samples of black slate containing significant (>5%) sulphide mineralization. On the basis of only two samples, a correlation between the sulphidic black slates and Hg concentration is not possible. Mercury concentrations for the nine rock samples collected during this study are significantly below the mean

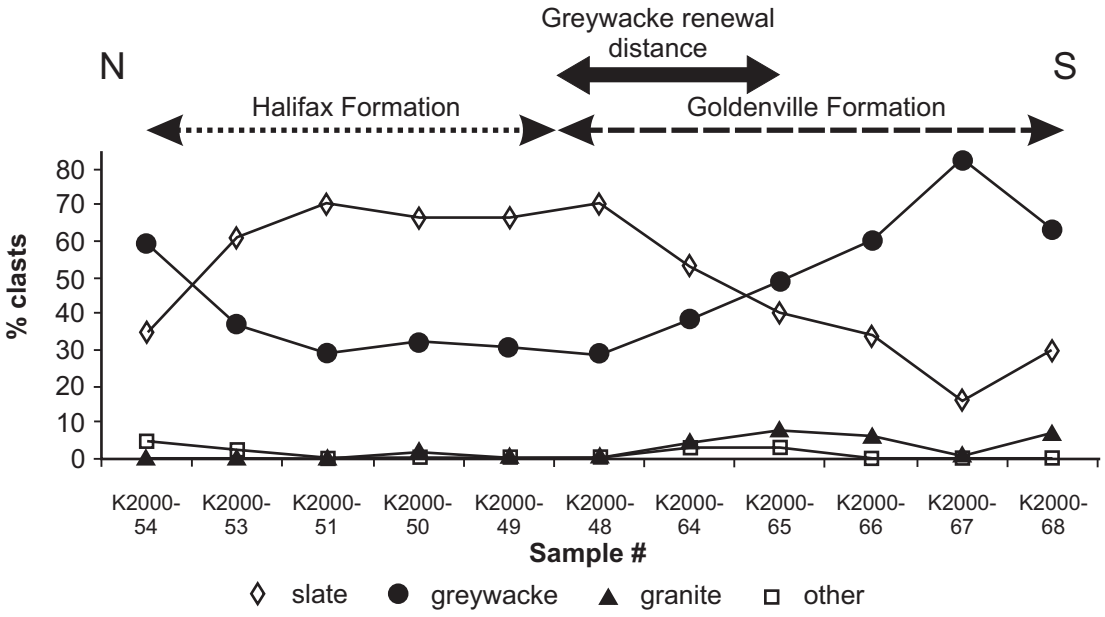

Fig. 3 Till clast counts (>4 mm) recovered from till samples collected along transect 2 and 3 and projected into the same profile. The distance between samples is approximately 200 m. The greywacke renewal distance is estimated to be approximately 900 m. Bedrock geology of the Goldenville and Halifax groups represented by large dashed and dotted arrows, respectively, at the top of the figure. The solid black arrow indicates the greywacke renewal distance (~900 m).

Hg content of quartzite (53 ppb) and schist (100 ppb) reported by Jonasson and Boyle (1972). Smith (2000) reported a slightly higher mean Hg concentration of 3.3 ppb for a broader suite of rock types.

Geophysics: ground magnetic survey

The GHTZ is in part characterized by increased magnetic susceptibility relative to the Halifax and Goldenville formations (King 1997). The GHTZ, therefore, is a unique magnetic marker horizon readily identifiable on both airborne and ground magnetic surveys. Interpreted results of the detailed total field ground magnetic survey indicate that the Halifax and Goldenville formations are characterized by magnetic responses of similar amplitude (Fig. 5). The GHTZ, however, has a higher magnetic response, typically 400–800 nT greater than either the Halifax or Goldenville formation. This anomalous magnetic signature of the GHTZ confirms that the unit is a unique magnetic marker horizon at both the local and regional scales. The magnetic response of the GHTZ when constrained by the bedrock and surficial mapping indicate the inferred contact between the Halifax and Goldenville formations in this area is 500 to 1000 m north of the mapped contact of Horne and Corey (1994).

Previous studies by Goodwin *et al.* (2000) indicated a possible spatial correlation between Hg in soil gas and the GHTZ. Therefore, identifying the exact location of the GHTZ is important when interpreting Hg concentrations in till. The estimated thickness (not true thickness) of the GHTZ is approximately 800 m based on the three transects.

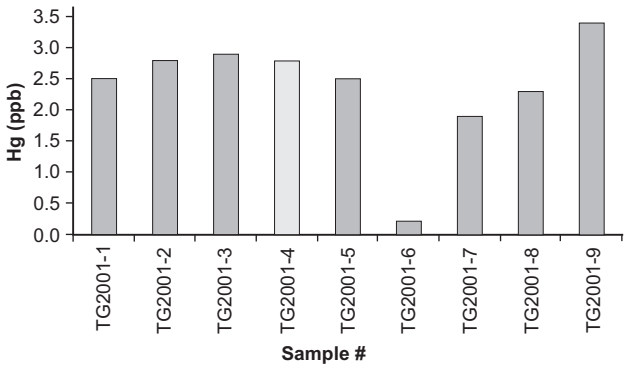

Fig. 4 Mercury concentrations (ppb) in rock samples from the study area. Range is 0.2 ppb – 3.4 ppb; mean 2.37 ppb; n=9; σ=0.91. Sample 4 is greywacke, all others are slate samples.

CONCLUSIONS

Sampling of both bedrock and glacial till in Kejimkujik National Park (KNP), southwestern Nova Scotia, indicates that

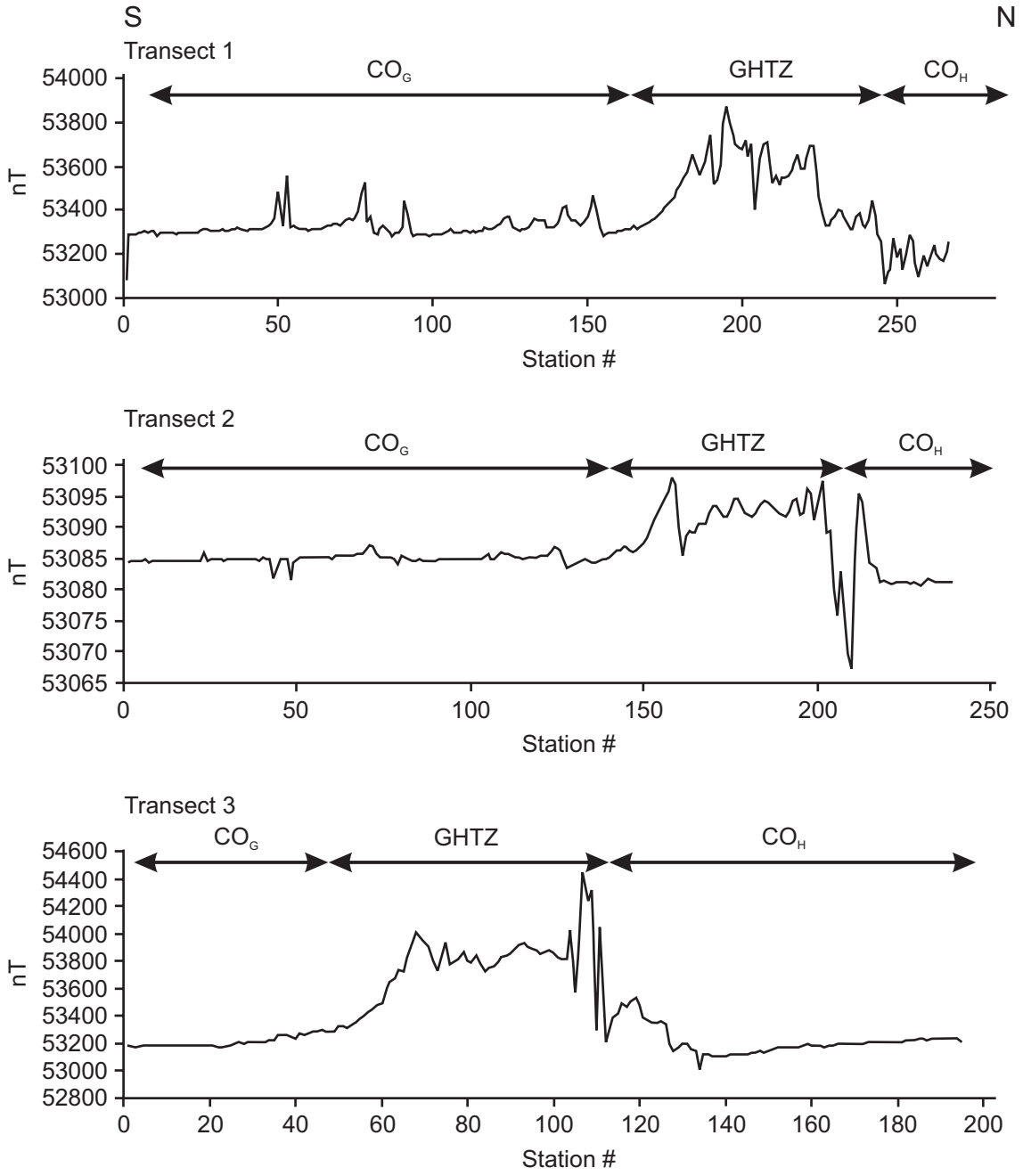

Fig. 5 Total field magnetic survey profiles along the three transects showing the interpreted position of the Goldenville Formation – Halifax Formation Transition Zone (GHTZ). Transects vary between 2.3 and 3.7 km in length with stations readings recorded at 12.5 m intervals. Bedrock geology consists of Goldenville Formation (CO_G), Halifax Formation (CO_H), and the Goldenville – Halifax Transition Zone.

Hg occurs naturally in both sample media. Overall, mean Hg in till concentrations for the Kejimkujik samples are slightly lower than mean Hg content for till reported by Jonasson and Boyle (1972) whereas the mean Hg concentrations in rock samples are significantly lower than mean Hg reported by Jonasson and Boyle (1972).

Mercury concentrations in till are the highest in the slate till facies (mean = 40.8 ppb) relative to the greywacke till facies (mean = 32.4 ppb). There is no obvious correlation between Hg and other analyzed elements that might indicate potential Hg source areas. Goodwin (2005) using a larger dataset (n=97) of till samples found that Hg exhibited a positive correlation with

Ga, Al, and, to a lesser degree, S. It remains unclear whether there is a correlation between increased Hg concentration and the GHTZ.

The Hg concentrations in slate and greywacke (mean = 2.4 ppb) are low but similar to previously reported values within KNP. One explanation is that the low Hg results are related to Hg released into till and the surrounding environment during weathering processes. Studies by Sangster *et al.* (2001) from drill core appear to confirm a possible link to increased Hg concentrations with depth. Although previous reports indicated higher levels of Hg in sulphidic black slates, the limited rock sampling completed for this study does not support that conclusion. Mercury concentrations are highest in the samples containing the most sulphide minerals (pyrrhotite and pyrite) but the values are too low (2.3 ppb to 3.4 ppb) to conclude that a correlation exists.

The total field ground magnetic survey and geologic mapping indicate that the geologic contact between the Goldenville Formation and Halifax Formation is 500 to 1000 m north of that shown on the most recent published maps. Till clast identification and counts support this conclusion and also suggest that the spatial extent of the Halifax Formation in the study area is smaller than displayed on the most recent geologic maps of the area.

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