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Amalgamated lake-sediment data from Quebec and Labrador, Canada

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Merging of geochemical datasets from neighbouring regions, compiled during differently administered programs, in order to create seamless geochemical maps is complicated due to factors such as differences in sampling methodologies and analytical protocols, and sample densities. In this study, a suite of 5,510 lake-sediment samples from western and northern Labrador has been re-analyzed by ICP-MS after *aqua-regia* digestion, in order to merge the results with a suite of 26,727 lake-sediment samples collected in an adjacent area of the province of Quebec, analyzed by the same method. This merging of datasets has enabled the creation of regional geochemical maps of a contiguous area in northeastern Canada of almost 300,000 km^2. This activity is one of several surficial geochemistry and mapping activities in northern Quebec and Labrador that form part of the Geological Survey of Canada's Geo-mapping for Energy and Minerals (GEM-2) Program (2013-2020) (McClenaghan *et al*. 2016). The purpose of this article is to report on the old and new lake-sediment datasets and about the ongoing production of new lake-sediment geochemical maps for the Quebec-Labrador region that will be published in the first half of 2017.

Samples

The Quebec lake-sediment samples were collected during six separate campaigns and have also been analyzed by various methods (Beaumier 1982; 1983; 1984a,b; 1985; 1986a-c; 1987a,b). Of those samples, however, it is only the 24,261 samples analyzed by ICP-MS after *Aqua-Regia* digestion by Acme Analytical Laboratories in Vancouver that were used for the data amalgamation (Maurice & Labbé, 2009). The Labrador samples were re-analyzed in 2015 by Bureau Veritas Mineral Laboratories (the successor company to Acme) and reported by McCurdy (2016) and McCurdy *et al*. (2016). These new data are for a subset of samples that are part of a total of 19,433 samples, which were collected over most of the territory as part of the National Geochemical Reconnaissance (NGR) program of the Geological Survey of Canada (Boyle *et al*. 1981; Hornbrook *et al*. 1983; Friske and Hornbrook 1991; Friske *et al*. 1993a-d, 1994). These lake-sediment samples were previously analyzed for a variety of elements by various methods and after various digestion methods, as well as by INAA (Table 1 - *See page 5*). Only the recent re-analyses by *Aqua Regia*/ICP-MS are considered here. There is general correspondence, between the Quebec and Labrador programs, in the analyzed elements and their lower detection limits (Table 2 - *See page 5*), although the detection limits for Au and Pt in the Quebec dataset are both 1 ppb, compared to 0.2 ppb and 2 ppb in the new Labrador dataset. Also, the Labrador samples were analyzed additionally for Dy, Er, Eu, Gd, Ho, Lu, Nd, Pr, Sm, Tb, Tm and Yb which are omitted from this study since there are no corresponding data for the Quebec samples.

While the sample coverage over Labrador and most of Quebec was fairly even at 6 to 8 samples/100 km^2, coverage over the southern part of the Labrador Trough (Fig. 1 - *See page 6*) in Quebec was at least four times as dense (Amor 2015). In order to provide even coverage over the study area, a random sub-selection of 25% of the samples was taken from the total collected in this higher-density area. Sub-selection was done independently within each NTS 1:50,000 map sheet, to avoid regions of over- or under-selection, or 'clumping', but the resulting coverage is still somewhat uneven compared to the remainder of the study area.

Geology

The area covered by the lake-sediment sampling is entirely underlain by Precambrian rocks of the Canadian Shield (Hoffman 1990; Wardle & Van Kranendonk 1996). It consists of a major zone of diachronous accretion and collision between three Archean-age crustal blocks: i) the Superior Craton (Archean), ii) the Core Zone (mostly Archean with earliest-Paleoproterozoic crust) and iii) the North Atlantic Craton (Archean), and intervening Paleoproterozoic-age supracrustal sequences and magmatic arcs (Fig. 1). The boundary between the Core Zone and North Atlantic Craton is the Torngat Orogen, a zone of high metamorphic grade and ductile, mostly dextral transcurrent shear formed at ca. 1.87-1.84 Ga (Wardle *et al*. 2002). The Torngat Orogen preserves an accretionary prism dominated by metapelites (Tasiuyak Gneiss) and the tectonically exhumed deep root of a ca. 1.87-1.86 Ga magmatic arc (Lac Lomier Complex). The Burwell Domain, exposed on the northern tip of Labrador, consists of ca. 1.89 Ga tonalites and charnockites emplaced in Archean-age crust (Scott & Machado 1995). On its western side, the Core Zone is

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Amalgamated lake-sediment data...

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Table 1: Summary of lake-sediment analyses for samples collected in Quebec and Labrador databases that were reported prior to current study.

Dataset	Digestion	Finish/Method	Number of Samples	Elements
Quebec	*Aqua regia*	ICP-ES	26497	Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Eu, Fe, Ga, Ge, In, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sc, Sm, Sr, Th, Ti, V, Y, Zn, Zr
	Aqua regia	ICP-MS	24261	Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, Sc, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr
	Multiacid (HNO_3-HCl-HF-$HClO_4$	ICP-MS	1869	Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tm, U, V, W, Y, Yb, Zn, Zr
	Aqua regia	AAS	17169 268 18116 12132	As Cr Hg Sn
		INAA	15393 - 15881	As, Au, Br, Cs, Sb, Se, Tm, U, W
		Gravimetry	26489	Loss on Ignition (L.O.I.)
Labrador	Multiacid (HNO_3-HCl HF-$HClO_4$)	ICP-ES	18357	Al, Ba, Be, Ca, Ce, Co, Cr, Cu, Dy, Fe, Ga, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Sc, Sr, Th, Ti, V, Y, Zn, Zr
	Aqua regia	AAS	19419 10364 19419 10364	Co, Cu, Fe, Mn, Ni, Pb, Zn Cd Mo V
	Aqua regia	Cold-vapour AAS	19296	Hg
	Aqua regia	Hydride AAS	18946 2449	As Sb
	Aqua regia	Colorimetry	4636	As
	K_2CO_3-KNO_3 fusion	Ion-specific electrode (ISE)	19259	Fluoride
		INAA	19196	As, Au, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Mo, Na, Ni, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, W, Yb
		Delayed neutron) counting (DNC	18763	U
		Gravimetry	19410	Loss on Ignition (L.O.I.)

Table 2: Lower Detection Limits (LDL) for aqua regia/ICP-MS determinations in this study. Analyses of Labrador samples also included Dy, Er, Eu, Gd, Ho, Lu, Nd, Pr, Sm, Tb, Tm and Yb. Detection limits for the Quebec and Labrador samples were 1 and 0.2 ppb respectively for Au, and 1 and 2 ppb for Pt.

		LDL				LDL				LDL	
Element	Units	Quebec	Labrador	Element	Units	Quebec	Labrador	Element	Units	Quebec	Labrador
Ag	ppm	0.002	0.002	Hf	ppm	0.02	0.02	S	pct	0.02	0.02
Al	ppm	100	100	Hg	ppb	5	5	Sb	ppm	0.02	0.02
As	ppm	0.1	0.1	In	ppm	0.02	0.02	Sc	ppm	0.1	0.1
Au	ppb	1	0.2	K	ppm	100	100	Se	ppm	0.1	0.1
B	ppm	20	20	La	ppm	0.5	0.5	Sn	ppm	0.1	0.1
Ba	ppm	0.5	0.5	Li	ppm	0.1	0.1	Sr	ppm	0.5	0.5
Be	ppm	0.1	0.1	Mg	ppm	100	100	Ta	ppm	0.05	0.05
Bi	ppm	0.02	0.02	Mn	ppm	1	1	Te	ppm	0.02	0.02
Ca	ppm	100	100	Mo	ppm	0.01	0.01	Th	ppm	0.1	0.1
Cd	ppm	0.01	0.01	Na	ppm	10	10	Ti	ppm	10	10
Ce	ppm	0.1	0.1	Nb	ppm	0.02	0.02	Tl	ppm	0.02	0.02
Co	ppm	0.1	0.1	Ni	ppm	0.1	0.1	U	ppm	0.1	0.1
Cr	ppm	0.5	0.5	P	ppm	10	10	V	ppm	2	2
Cs	ppm	0.02	0.02	Pb	ppm	0.01	0.01	W	ppm	0.1	0.1
Cu	ppm	0.01	0.01	Pd	ppb	10	10	Y	ppm	0.01	0.01
Fe	ppm	100	100	Pt	ppb	1	2	Zn	ppm	0.1	0.1
Ga	ppm	0.1	0.1	Rb	ppm	0.1	0.1	Zr	ppm	0.1	0.1
Ge	ppm	0.1	0.1	Re	ppb	1	1				

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separated from the Superior Craton by the ca. 1.83-1.79 Ga New Quebec Orogen (Clark & Wares 2005). This predominantly transpressional orogen consists of greenschist- to lower-amphibolite facies clastic and chemical sedimentary rocks representing i) autochthonous rift-to-drift sequences, as well tectonically overlying flysch, banded iron-formation and molasse sediments interlayered with minor volcanic rocks (Kaniapiscau Supergroup), ii) belts composed predominantly of mafic volcanic rocks and sills interlayered with sediments comprised mostly of meta-siltstone and black shale (Baby-Howse and Doublet domains) with the Doublet interpreted as remnant of a back-arc basin (Rohon *et al.* 1993), and iii) Mid- to upper-amphibolite facies, Paleoproterozoic-age clastic metasedimentary and minor mafic metavolcanic rocks that are in thrust contact with the Baby-Howse and Doublet zones in basement-involved thick-skinned tectonics (Rachel-Laporte zone). Rocks of the Baby-Howse and Doublet zones are intruded by voluminous, ca. 1.88 Ga metagabbro sills of the Montagnais suite. Based on continuity of regional aeromagnetic patterns, Archean crust occurring in basement windows and east of the Labrador Trough is interpreted to have Superior Craton affinity; that hypothesis, however, remains to be tested. The Core Zone is also host to a ca. 1.84-1.81 Ga continental magmatic arc, the De Pas Batholith (Dunphy & Skulski 1996).

The southeastern portion of the map presented in Figure 1 is intruded by voluminous Mesoproterozoic-age plutons, including the Nain Plutonic Suite, emplaced between ca. 1.46 and 1.29 Ga (Emslie & Stirling 1993; Amelin *et al*. 1999). The latter are economically important, being host to the Voisey's Bay magmatic Ni-Cu deposit as well as the Strange Lake REE deposit. The southernmost extent of the lake sediment survey, east of the Smallwood Reservoir, covers the Seal Lake Group, a set of ca. 1.25 Ga volcano-sedimentary sequences with low-grade metamorphic overprint that contains numerous copper occurrences (van Nostrand & Corcoran 2013). The study area is bounded to the south by the Grenville Orogen.

Comparison of Quebec and Labrador Analyses

The application of the same methods of digestion and analysis to both suites of samples greatly facilitates the merging of data from the two jurisdictions, despite their having been collected and analyzed at different times, and as part of two separately administered programs. There are no paired analyses (from the Quebec and Labrador programs) of the same samples, with which to establish rigorously the relationship between the two programs. Instead, to verify the closeness of the correspondence, analyses of samples from the Quebec dataset, collected close to the border between the two jurisdictions, have been paired with their 'nearest neighbours' on the Labrador side. In all cases, the paired samples were separated by a distance of 2 km or less; they have been separated into high-loss on ignition (LOI) and low-LOI datasets, using a threshold of 18.4%. This threshold was arrived at by examining the behaviour

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Amalgamated lake-sediment data... continued from page 6

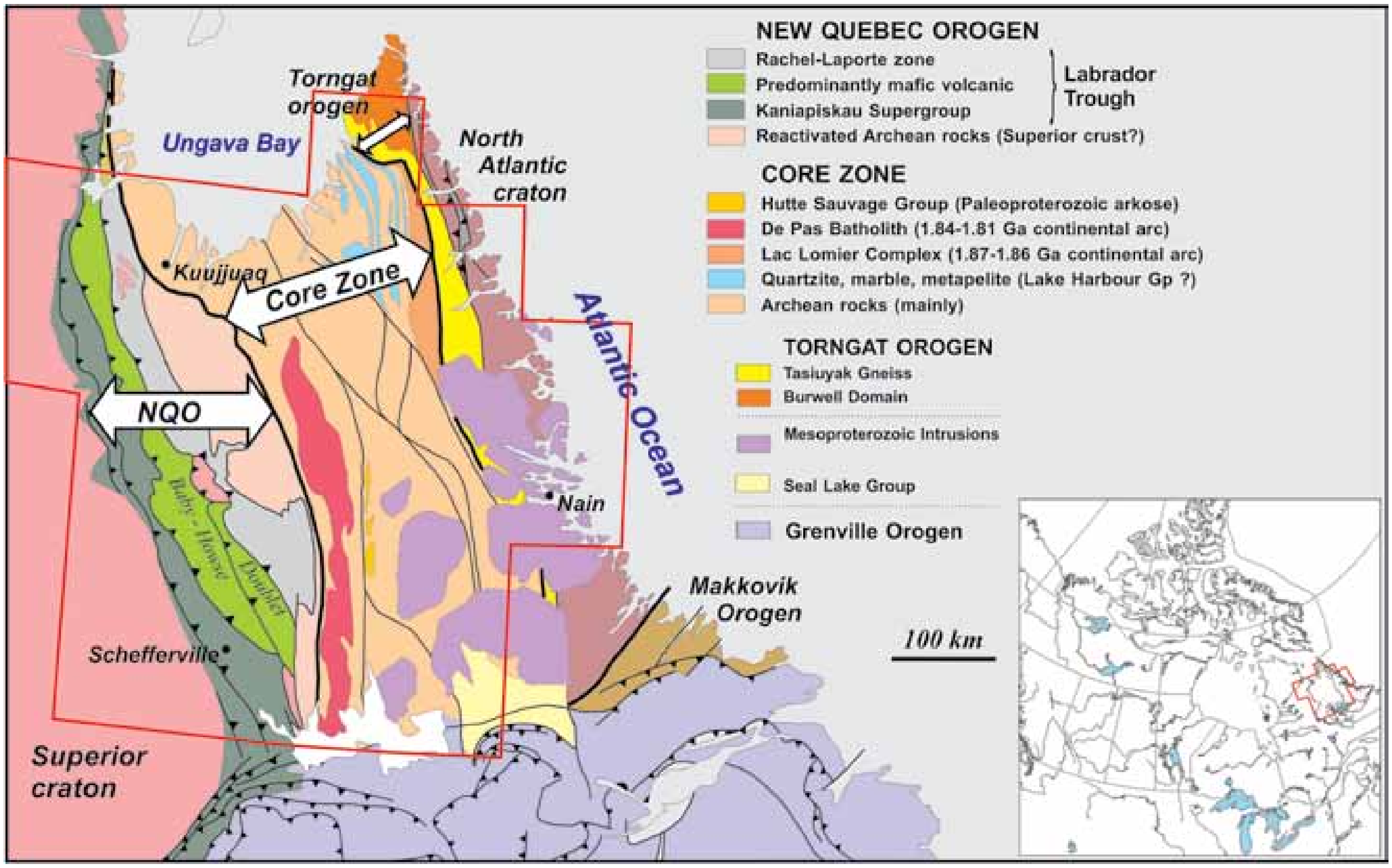

Figure 1: Simplified geological map of the Precambrian Shield in Quebec and Labrador. Modified after James et al. (2003). Study area outlined by red box.

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of a variety of elements with increasing LOI content in the Quebec and Labrador samples (Fig. 2), and corresponds

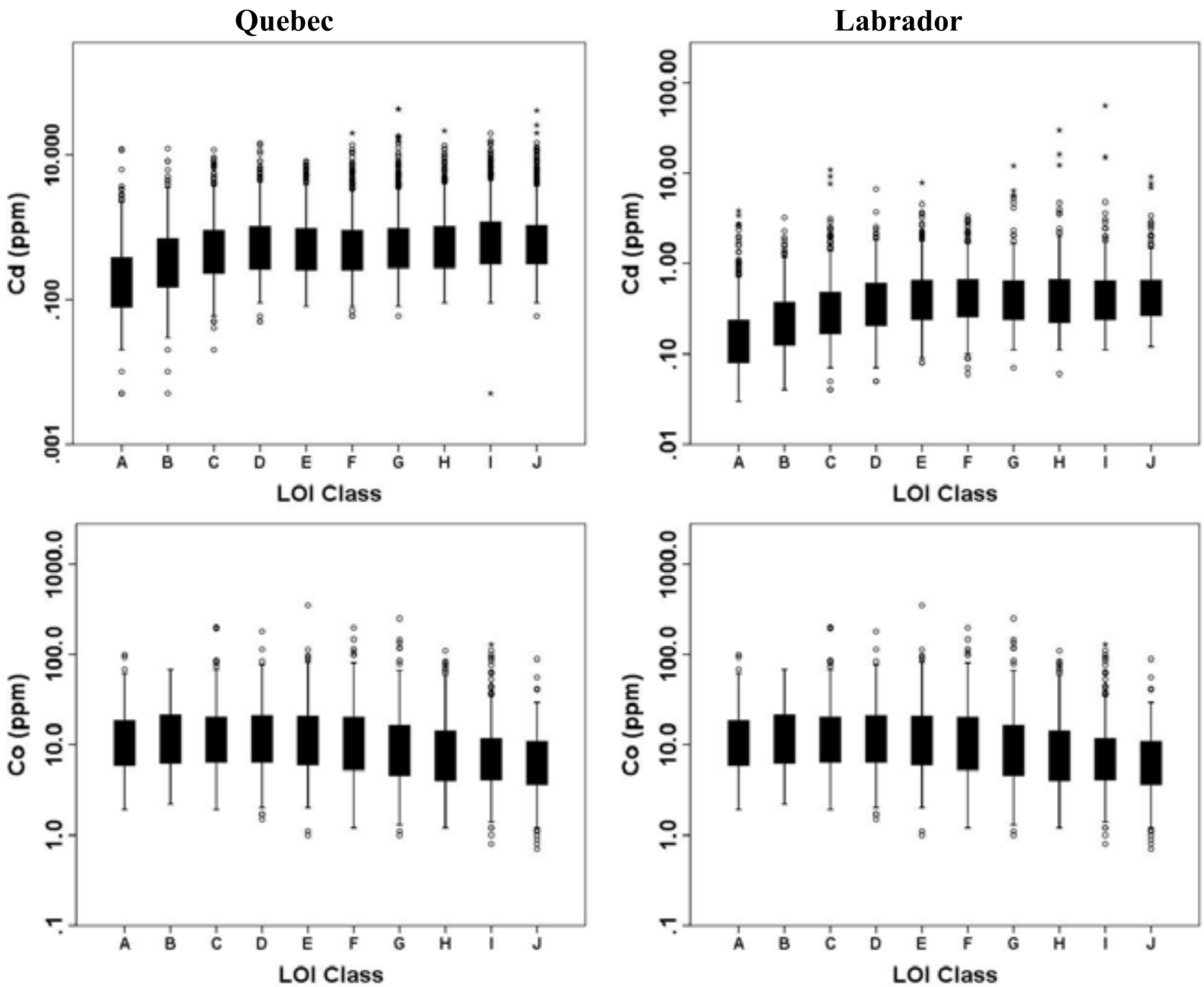

Figure 2: Relationship between loss-on-ignition (LOI) and Cd and Co content of lake sediment in NE Quebec and Labrador. LOI classes: A: ≤ 6.2%; B: 6.3-10.4%; C: 10.5-14.4%; D: 14.5-18.4%; E: 18.5-22.6%; F: 22.7-26.4%; G: 26.5-29.8%; H: 29.9-33.8% I: 33.9-54%;J: >54%. Many (though not all) elements show a similar inflection point between 18 and 22% LOI.

closely to a cutoff arrived at similarly by Trépanier (2007).

Application of paired t-tests (R-Project, 2016), following $\log_{10}$ transformations, to these high and low-LOI subsets, and both subsets combined, led to the conclusion that if attention was restricted to sample pairs separated by distances of 2 km or less, there was no significant difference (indicating a 'background shift') between analyses of Al, Ba, Cd, Co, Cr, Cu, Fe, Hg, K, La, Li, Mg, Mo, Ni, Pb, Rb, S, Sr, Th, Ti, U or V in the Labrador and Quebec datasets at the 95% confidence level. In the case of Be, Ca, Ce, Cs, Ga, Mn, Nb, P, Sc, Se, Sn, Tl, V, Zn and Zr, at least one (but not all three) of the paired t-tests showed no significant differences. Only Ag showed significant differences in all three tests. More than 10% of the analyses of As, Au, Ge, Hf, In, Re, Sb, Te and W were less than the lower detection limit in all six datasets and are not amenable to statistical calculations of this kind; nevertheless, map plots of some of these elements are instructive.

An alternate procedure used the average difference between the pairs in $\log_{10}$ units; this was then anti-logged and the difference from unity (equivalent to zero difference between the logarithms) was expressed as a percentage. Where the difference was ≤10%, the element was deemed acceptable for mapping, and where >10% and ≤15% the element was deemed acceptable with caveats. Based on the ≤10% criterion the following elements would be 'mappable': Al, Ba, Be, Cd, Cu, Hg, Mg, Ni, Pb, S, Sr, Th, Ti, and U. Relaxing the criterion to ≤15% allowed for these additional elements to be mappable: Ca, Cr, Fe, Ga, Hf, K, La, Li and, Y.

Geochemical Plots

Figures 3 to 7 show the aerial distribution of values of K, U, Pb, S and Cu in the combined datasets. These elements were chosen because they are each loaded significantly in different principal components extracted from each of the four datasets (Quebec / Labrador / high LOI / low LOI) and are therefore probably representative of the dominant processes affecting the distribution of the elements over the

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Amalgamated lake-sediment data... *continued from page 11*

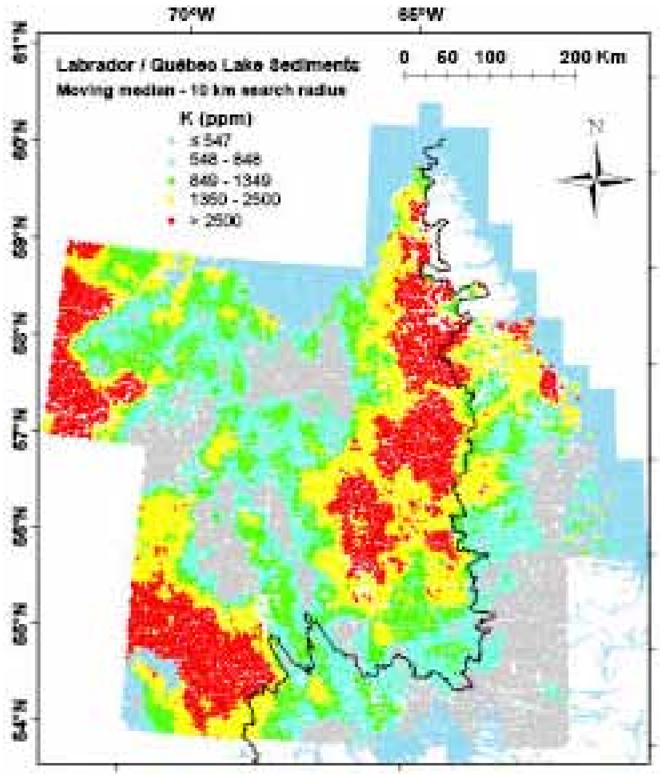

Figure 3: Distribution of K (unweighted moving medians) in Labrador and NE Quebec lake sediments.

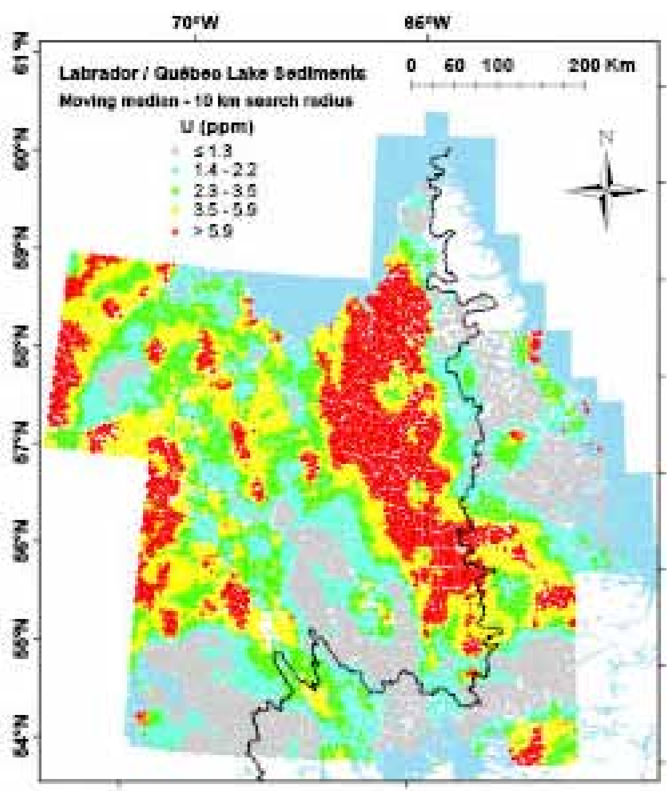

Figure 4: Distribution of U (unweighted moving medians) in Labrador and NE Quebec lake sediments.

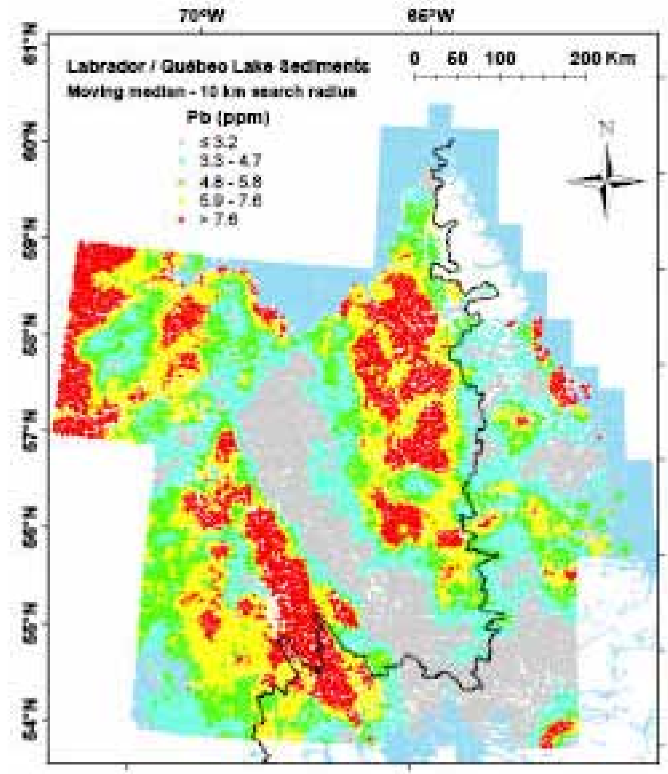

Figure 5: Distribution of Pb (unweighted moving medians) in Labrador and NE Quebec lake sediments.

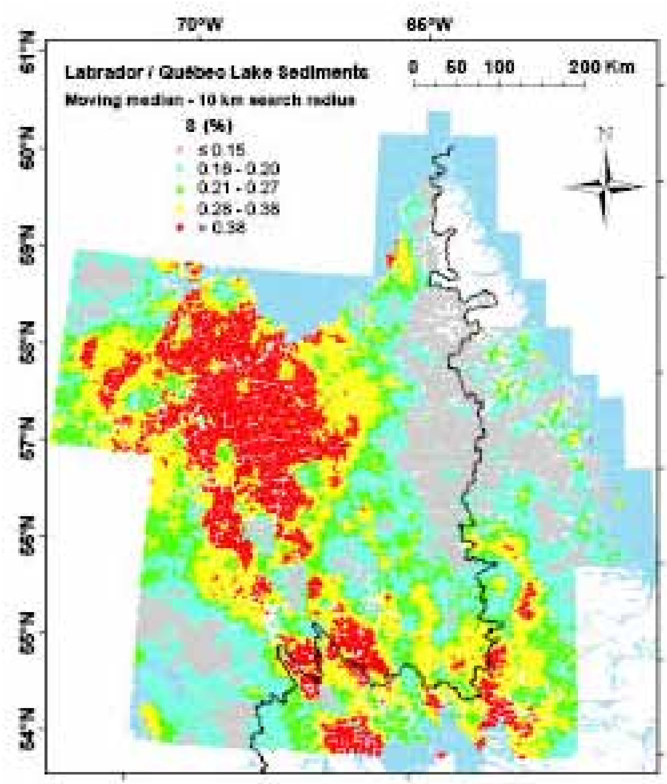

Figure 6: Distribution of S (unweighted moving medians) in Labrador and NE Quebec lake sediments.

entire region. The plotted value assigned to each sample is a moving unweighted median (Gustavsson *et al*. 2001) of all values of samples falling within a 10-km radius; this has the effect of smoothing the data while preserving the sample locations. In all cases the data are divided into five quintile class intervals; that is to say, the samples assigned to each colour make up 20% of

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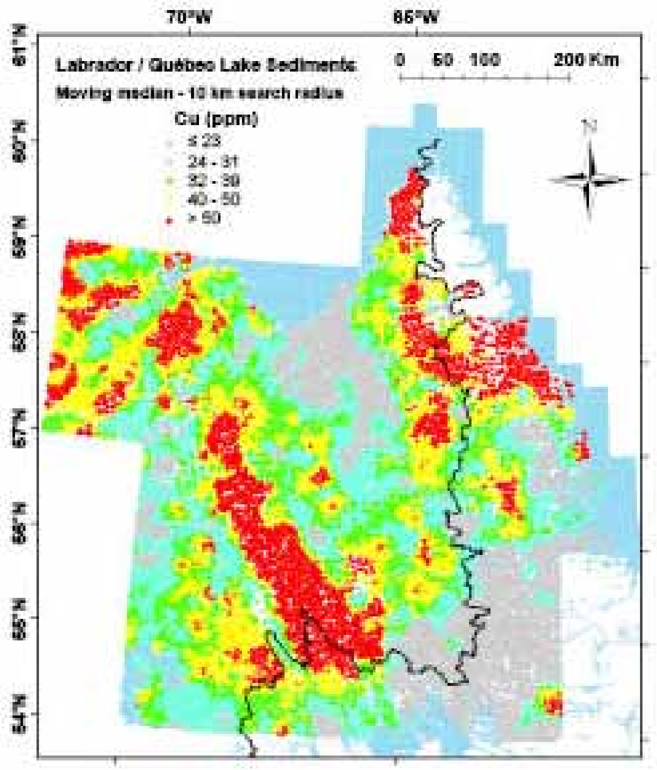

Figure 7: Distribution of Cu (unweighted moving medians) in Labrador and NE Quebec lake sediments.

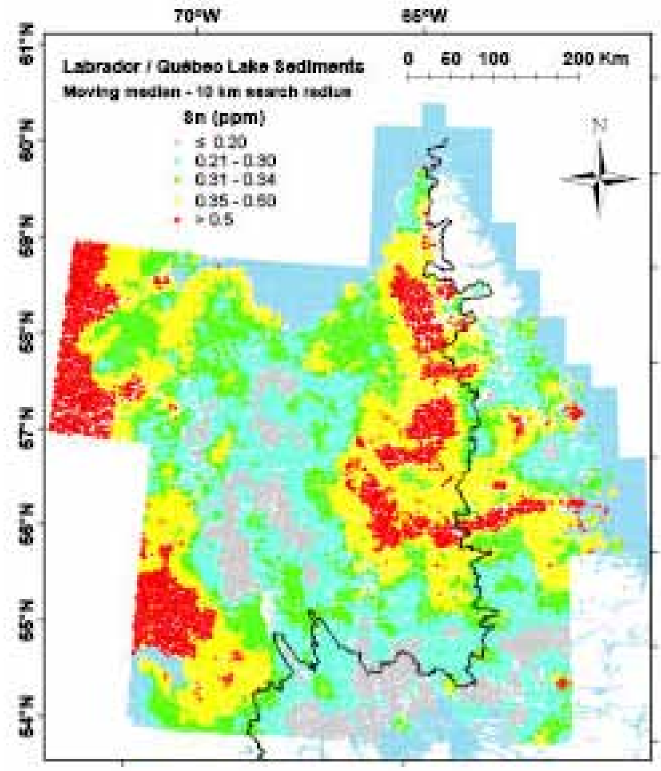

Figure 9: Distribution of Sn (unweighted moving medians) in Labrador and NE Quebec lake sediments.

the total. Figures 8 and 9 show the distribution of Sb and Sn, whose areal distributions display a number of interesting features.

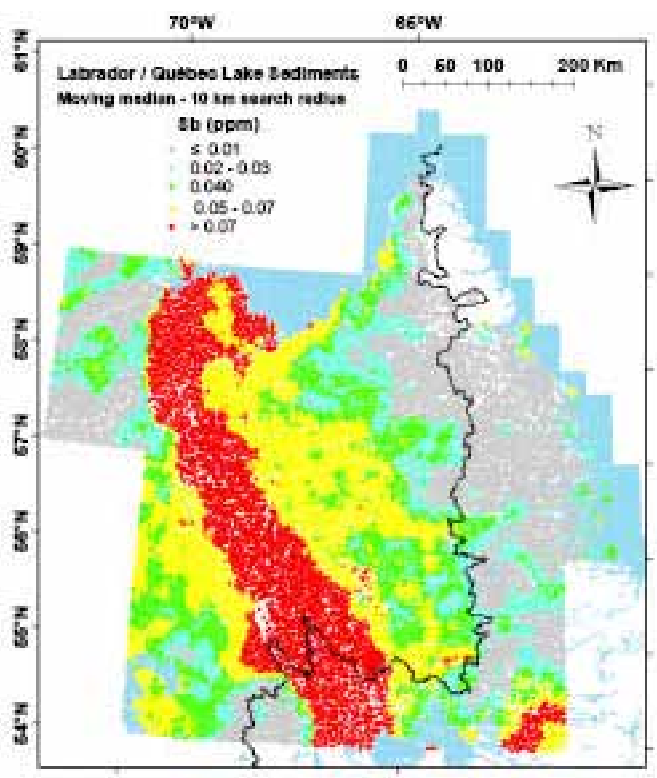

Figure 8: Distribution of Sb (unweighted moving medians) in Labrador and NE Quebec lake sediments.

Levelling between Quebec and Labrador datasets

Results of the paired t-tests described above suggest that there is very little need for levelling of the two datasets. Therefore, the datasets can be combined without a serious discontinuity appearing at the provincial border (e.g., Amor 2015). One exception to this generalization is Ag; therefore the data from Labrador for this element have been levelled using regression equations derived for nearest-neighbour pairs, separated into high-LOI (>18.4%) and low-LOI groups. Results are shown in Figures 10a and 10b.

In the dataset from Quebec, an internal levelling issue is apparent for Cd and Hg, with samples from project 1997520 showing significantly higher values of the first element, and lower values of the second, than in samples from projects 1983050, 1983055 and 1984059. This results in a linear discontinuity along the east-west boundary of project 1997520's area of coverage (Figs. 11a, b). A nearest-neighbour regression exercise was carried out on these data and the results are shown in Figures 12a and 12b.

Conclusion

Multi-element (ICP-MS) analyses of lake sediments from adjacent parts of northeastern Quebec and Labrador, that were collected over an area of approximately 300,000 km^2, were merged to create geochemical maps of this large area. Though the analyses were carried out under different programs at different times, there were no levelling issues between the two datasets for most elements, although levelling was necessary for Cd and Hg within the Quebec

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Amalgamated lake-sediment data... *continued from page 13*

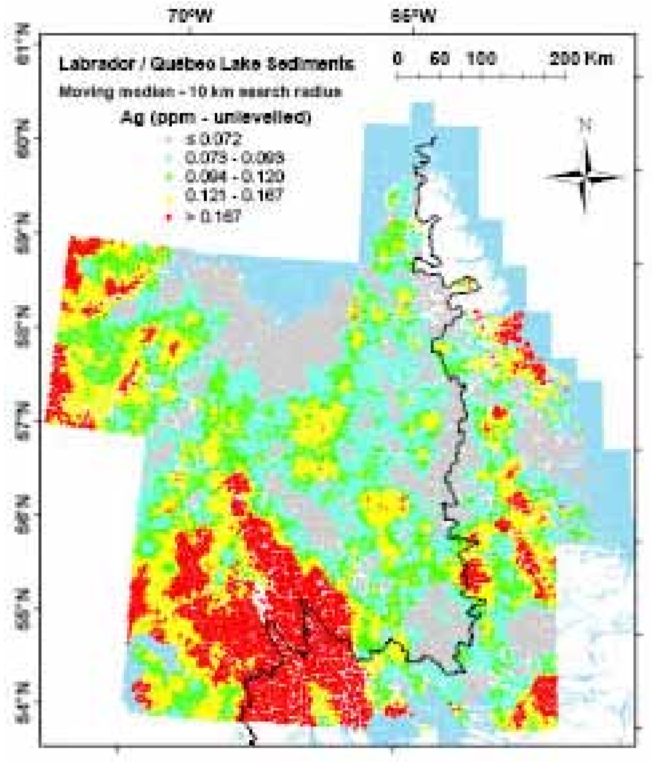

Figure 10a: Distribution of unadjusted Ag (unweighted moving medians) in Labrador and NE Quebec lake sediments.

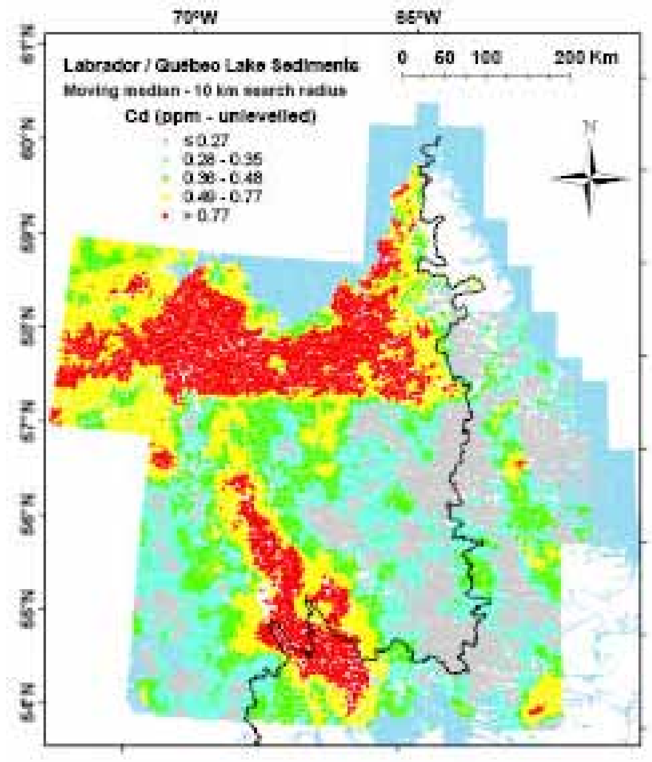

Figure 11a: Distribution of unadjusted Cd (unweighted moving medians) in Labrador and NE Quebec lake sediments.

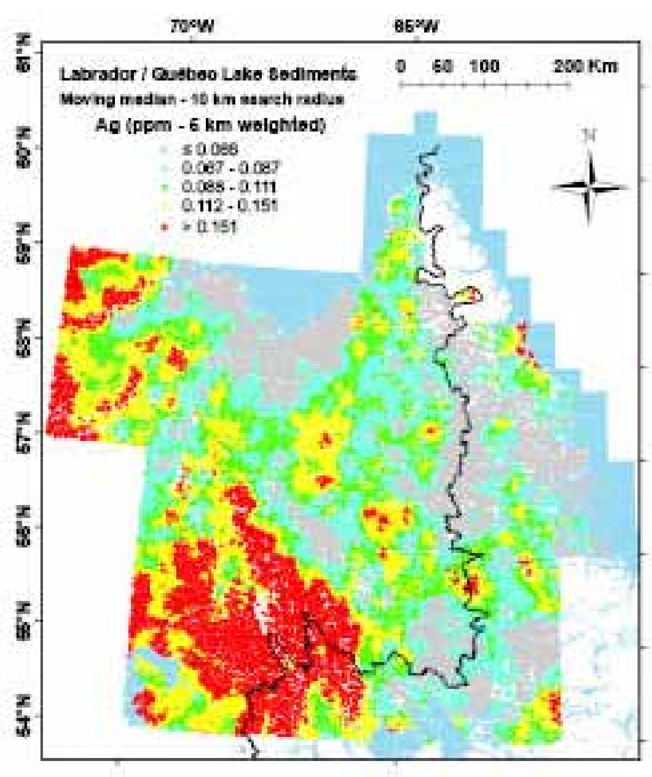

Figure 10b: Distribution of levelled Ag (unweighted moving medians) in Labrador and NE Quebec lake sediments.

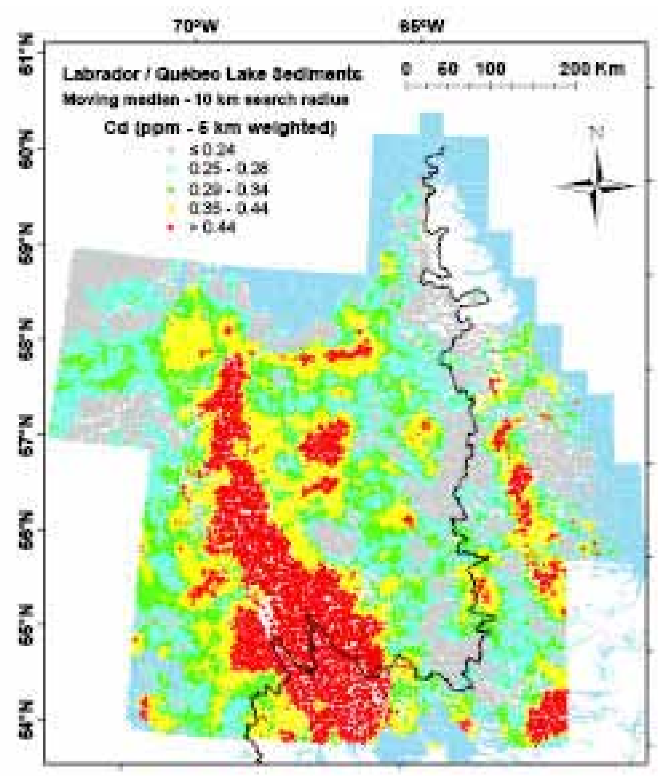

Figure 11b: Distribution of levelled Cd (unweighted moving medians) in Labrador and NE Quebec lake sediments.

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Amalgamated lake-sediment data... *continued from page 14*

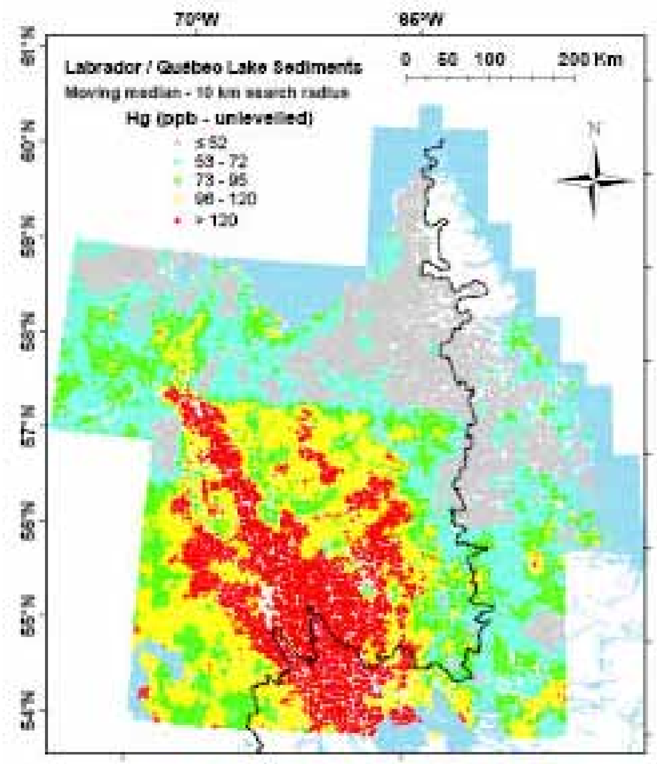

Figure 12a: Distribution of unadjusted Hg (unweighted moving medians) in Labrador and NE Quebec lake sediments.

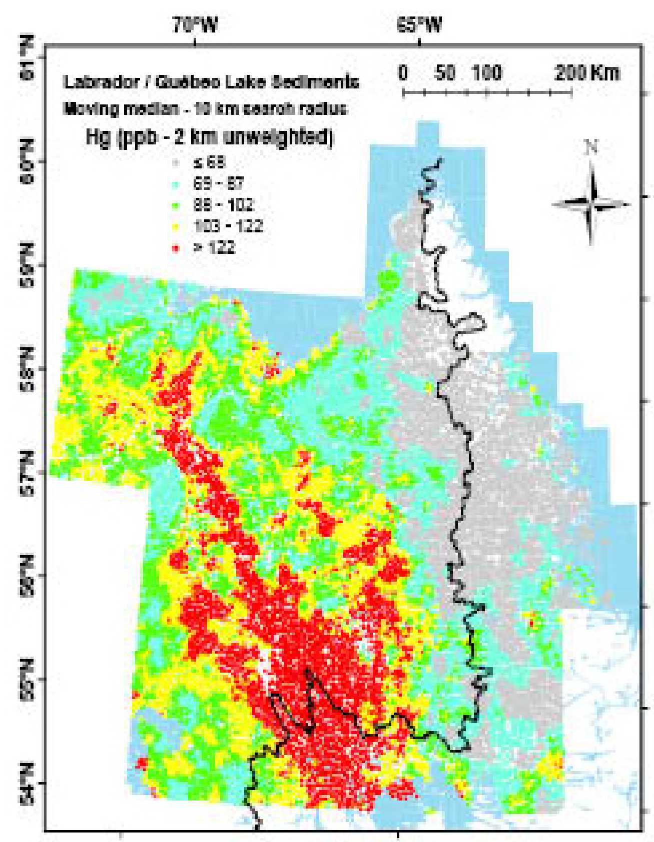

Figure 12b: Distribution of levelled Hg (unweighted moving medians) in Labrador and NE Quebec lake sediments.

dataset. Application of unweighted moving medians, and 5-colour quintile class intervals, has resulted in maps clearly showing a variety of broad geochemical features.

The most distinctive geochemical feature is related to the 1,100 km long, iron-ore bearing Labrador Trough of the New Quebec Orogen, which has elevated values of Cu, and other elements including Sb and As, over about half of its strike length, starting at the Smallwood Reservoir in the south and extending to Ungava Bay in the north. Other known geological features with a distinct signature in the composition of the lake sediments include the rocks of the Seal Lake Group in the southeastern corner of the study area; this area hosts host Cu mineralization and lake sediments display elevated values of U, Sb, Ag and Cd, amongst other elements.

In conclusion, the merging of the two datasets has been achieved with very few difficulties and it is hoped that the merged data will create an added stimulus to mineral exploration in both Quebec and Labrador.

Acknowledgements

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