

Till, stream sediment, and stream water geochemical signatures of intrusion-hosted Sn-W deposits: examples from the Sisson W-Mo and Mount Pleasant Sn-W-Mo-Bi-In deposits, New Brunswick

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Abstract: Indicator minerals methods for intrusion-hosted Sn and W deposits were tested at the intrusion-hosted Sisson W-Mo and Mount Pleasant Sn-W-Mo-Bi-In deposits in eastern Canada as part of the Geological Survey of Canada's (GSC) Targeted Geoscience Initiative 4 (TGI 4). The program was a collaborative federal geoscience program with a mandate to provide industry with the next generation of geoscience knowledge and innovative techniques that will result in more effective targeting of buried mineral deposits. The case studies are a collaborative effort between the GSC, the New Brunswick Department of Energy and Mines (NBDEM), and the holders of the Sisson (Northcliff Resources Limited, Hunter Dickinson Inc.) and the Mount Pleasant (Adex Mining Inc.) deposits, and Laurentian University.

The detailed till mineralogical + geochemical study described here is one of the first reported for major Sn-W deposits in glaciated terrain. Indicator minerals were examined in heavy mineral (>3.2 specific gravity) concentrates of bedrock and till samples from both deposits, as well as in stream sediment samples from the Sisson deposit area. The <0.063 mm fraction of till samples from both deposits was analysed geochemically using modified aqua regia (partial) and borate fusion (total) digestions.

Indicator/pathfinder trace elements in till at the Sisson W-Mo deposit includes W, Mo, Cu, Zn, Pb, Ag, Bi, In, As, Cd, Zn, and Te. Indicator/pathfinder trace elements in till at the Mount Pleasant Sn-W-Mo-Bi-In deposit includes Sn, W, Mo, Bi, In, Ag, As, Cd, Cu, Pb, Re, Te, Tl, and Zn. These element suites reflect the polymetallic nature of these deposits and the broader suite of elements that is now available using modern analytical methods such as inductively coupled plasma – mass spectrometry. The Mount Pleasant deposit is a significant source of indium and till down ice of the deposit contains some of the highest indium values (13 ppm) ever reported for till, indicating that till geochemistry can be an important exploration tool for In-bearing deposits. Indicator/pathfinder elements in stream sediment downstream of the Sisson deposit include W, Mo, Ag, As, Bi, Cd, Cu, In, Tl, and Zn. Indicator/pathfinder elements in stream water around the Sisson deposit include W, Mo, As, Cd, Cu, Cs, and Zn.

Indicator minerals of the Sisson deposit identified in the 0.25-0.5 mm fraction of mineralised bedrock, till, and stream sediments include scheelite, wolframite, molybdenite, chalcopyrite, Bi minerals (joseite, native Bi, bismutite, bismuthinite), galena, sphalerite, arsenopyrite, spessartine, pyrrhotite, and pyrite. Indicator minerals of the Mount Pleasant deposit identified in the 0.25-0.5 mm fraction of mineralised bedrock and till include cassiterite, wolframite, molybdenite, topaz, fluorite, galena, sphalerite, chalcopyrite, galena, arsenopyrite, pyrite, and loellingite. Additional but rare secondary indicator minerals of the Mount Pleasant deposit include beudantite, anglesite, and plumbogummite which formed by oxidation and weathering of the galena.

The extensive suite of indicator minerals for both deposits reflects their polymetallic natures and the ability of modern indicator mineral methods to recover these minerals. Indicator minerals present in the coarse (0.5-2.0 mm) heavy mineral fraction of till indicate proximity to the mineralised source. A commercial service is now available to systematically determine the scheelite contents of heavy mineral concentrates using its short wave ultraviolet light fluorescence. This service will provide consistent scheelite results within, and between, heavy mineral sampling surveys. Fluorite abundance was shown to be most abundant in the 3.0-3.2 SG (mid-density) fraction of till and can be readily recovered by including a mid-density heavy liquid separation as part of the processing procedures.

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Introduction

Few case studies have been conducted around significant Sn and W deposits to identify their indicator mineral and geochemical signatures in glaciated terrain. The Sisson W-Mo and Mount Pleasant Sn-W-Mo-Bi-In deposits (Fig. 1) in eastern Canada provide ideal sites to test/demonstrate these exploration methods for intrusion-hosted Sn and W deposits. These deposits were chosen because: (1) their bedrock geology is well known; (2) mineralisation was exposed to glacial erosion and they are till covered; and, (3) till geochemical dispersal trains have already been identified down ice from the deposits and thus, zones where metal-rich till occurs at surface are defined and can be targeted for indicator mineral sampling. The two studies were carried out as part of the Geological Survey of Canada's (GSC) Targeted Geoscience Initiative 4 (TGI 4) Program, a collaborative federal geoscience initiative with a mandate to provide industry with the next generation of geoscience knowledge and innovative techniques that will result in more effective targeting of buried mineral deposits. The case studies are a collaborative effort between the GSC, the New Brunswick Department of Energy and Mines (NBDEM), and the holders of the Sisson (Northcliff Resources Limited, Hunter Dickinson Inc.) and the Mount Pleasant (Adex Mining Inc.) deposits, and Laurentian University.

The purpose of this report is to provide an overview of the indicator mineral and geochemical research results for the two deposits. Detailed results are reported in the GSC open files, field guide, and journal paper listed in Table 1. Both deposits are located in the west-central part of New Brunswick and are hosted in Late Silurian to Early Devonian plutonic rocks that form a northeast-trending belt underlying the Miramichi Highlands in central New Brunswick (Fig. 1). In related TGI 4 studies, the GSC also studied indicator mineral and till geochemical signatures for porphyry Cu-Mo-Au deposits in central British Columbia. These results are also reported in this volume (Plouffe and Ferbey, 2015).

Sisson deposit geology

The bedrock geology of the Sisson deposit area is summarized below from Nast and William-Jones (1991), Marr (2009), Fyffe et al. (2008, 2010), Rennie et al. (2013), and Bustard et al. (2013). The deposit occurs at the eastern contact of the Nashwaak Granite and Howard Peak Granodiorite plutons (Fig. 2). The Howard Peak Granodiorite grades eastward into, and becomes intermixed with, gabbro. Granite dykes that are likely offshoots of the Nashwaak Granite transect

both the gabbro and granodiorite. East of the Howard Peak Granodiorite are Ordovician Tetagouche Group rocks that include the Turnbull Mountain Formation tuffaceous volcanic and sedimentary rocks, Hayden Lake Formation pyritiferous black shale intercalated with felsic volcanic rocks, and Push and Be Damned Formation mafic volcanic rocks, wacke and shale. Also to the east are the Cambro-Ordovician Miramichi Group quartzite and shale of the Knights Brook Formation.

The Sisson deposit is a bulk tonnage W-Mo intrusion-related deposit that consists of four wide and steeply dipping zones of vein and fracture-controlled W and Mo mineralisation that straddle the strongly sheared eastern contact of the Howard Peak Granodiorite (Figs. 2, 3). Mineralisation is likely related to the presence of a buried granitic stock at depth, which was the heat source for a hydrothermal system and metals. The deposit has elevated concentrations of Cu, Zn, Pb, Bi, and As that are directly related to late quartz-scheelite and sulphide-rich veins. Ore minerals in the deposit include scheelite, minor wolframite, and molybdenite. Other sulphide, oxide and telluride minerals present are listed in Table 2. The Nashwaak occurrence is a small high-grade Pb-Zn-Ag-Sb zone (Fig. 2) that subcrops under thin till cover approximately 900 m east of the Sisson deposit. This occurrence was originally interpreted as a volcanogenic massive sulphide showing but more recently has been interpreted to be a vein-type showing related to the Sisson mineralising system (Marr, 2009; Rennie et al., 2013).

Bedrock outcrops on the Sisson property and surrounding area are rare due to the locally thick and continuous cover of till. Till thickness varies from <2 m to 20 m over the deposit, and is on average 8 m thick. Surface till in the area consist mainly of sandy Early Wisconsinan lodgement till likely deposited by southeast glacial flow during the Caledonia Phase, and possibly reworked by south-southwest glacial flow during the Middle to Late Wisconsinan (Escuminac Phase). This till is discontinuously overlain by up to 2.5 m thick, loose, very sandy till deposited by westward flowing ice during the late-glacial Collins Pond Phase (Younger Dryas) (Seaman and McCoy, 2008; Seaman, 2009; Fyffe et al., 2010; Stea et al., 2011).

As part of a reconnaissance-scale till geochemical survey of central New Brunswick, Lamothe (1992) identified a 10 km long glacial dispersal train trending southeast from the Sisson deposit that was best defined by W, Cu, Pb, Zn, and Mo contents in till. More recently, Seaman (2001, 2002, 2003, 2007, 2012) and Seaman and McCoy (2008) identified elevated concentrations of W, As, Bi, Cd, Cs, Cu, In, Mo, Sn, and Zn in till up to 40 km southeast of the deposit. This glacial dispersal train is discontinuous in places due to local reworking during subsequent Late Wisconsinan glacial phases.

Table 1 – List of publications reporting indicator mineral and till geochemical data for the TGI-4 Sisson and Mount Pleasant deposit case studies: GSC open files, one journal paper, and one field trip guide book.

Deposit	Publication	Source	Content
Sisson	GSC Open File 7387	McClenaghan et al., 2013b	raw indicator mineral data for bedrock, till, stream sediment samples
Sisson	GSC Open File 7430	McClenaghan et al., 2013c	till geochemical data
Sisson	GSC Open File 7431	McClenaghan et al., 2013a	interpretation of indicator mineral data for bedrock samples
Sisson	GSC Open File 7467	McClenaghan et al., 2014c	interpretation of indicator mineral data for till samples
Sisson	GSC Open File 7756	McClenaghan et al., 2015c	geochemical & indicator mineral data for stream sediment and water samples
Sisson	NBDEM Field Guide	Thorne et al., 2014	Sisson field trip guide
Sisson	Atlantic Geology	McClenaghan et al., 2014b	interpretation of till geochemical data
Mount Pleasant	GSC Open File 7573	McClenaghan et al., 2014a	raw indicator mineral data for bedrock and till samples
Mount Pleasant	GSC Open File 7721	McClenaghan et al., 2015a	interpretation of indicator mineral data for bedrock samples
Mount Pleasant	GSC Open File 7722	McClenaghan et al., 2015b	till geochemical data
Mount Pleasant	GSC Open File 7804	McClenaghan et al., in press	interpretation of indicator mineral data for till samples

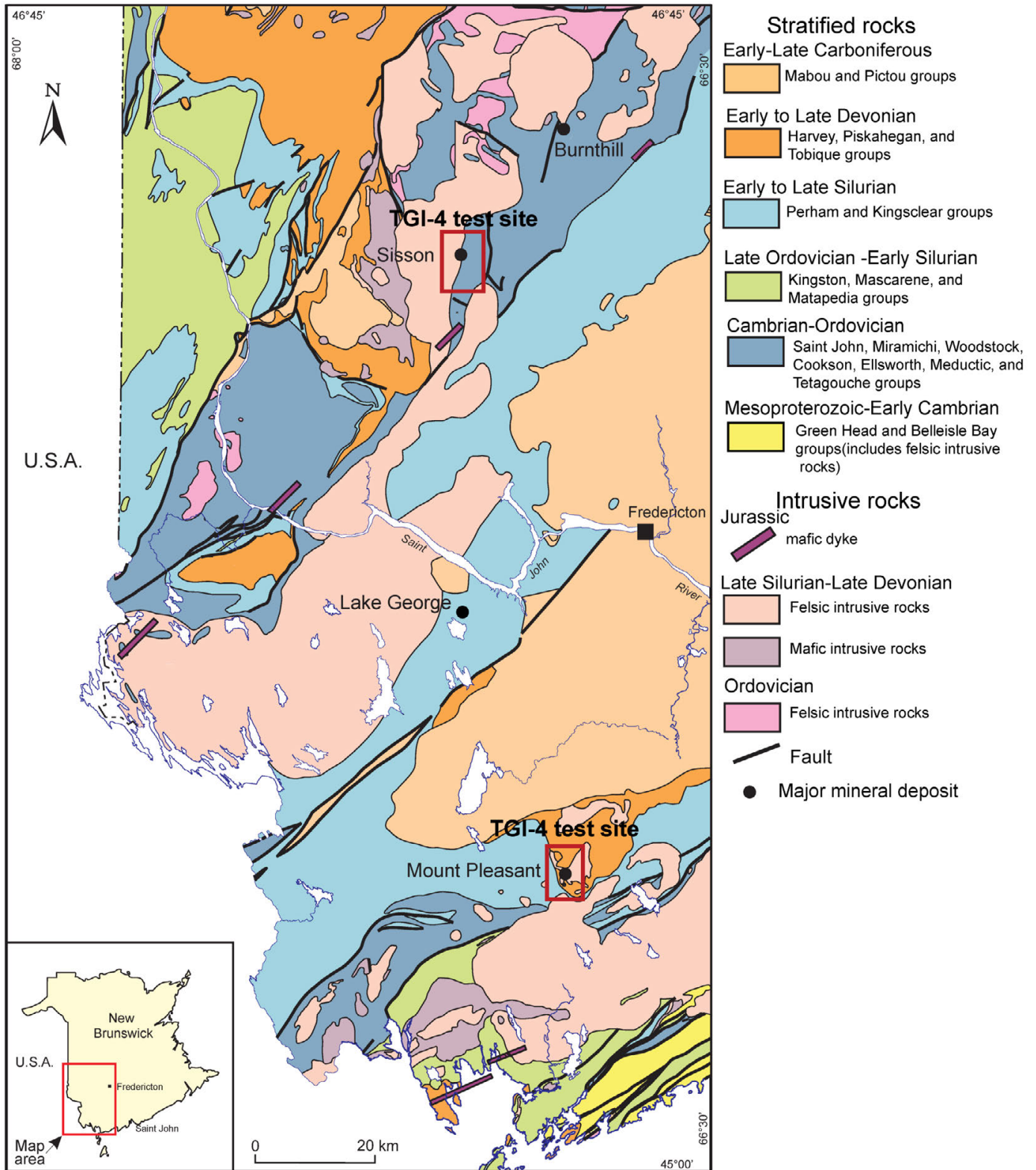


Figure 1 – Bedrock geology of west-central and southern New Brunswick showing the location of the Sisson W-Mo deposit, the Mount Pleasant Sn-W-Mo-Bi-In deposit, and other intrusion-hosted deposits (modified from Fyffe et al., 2010).

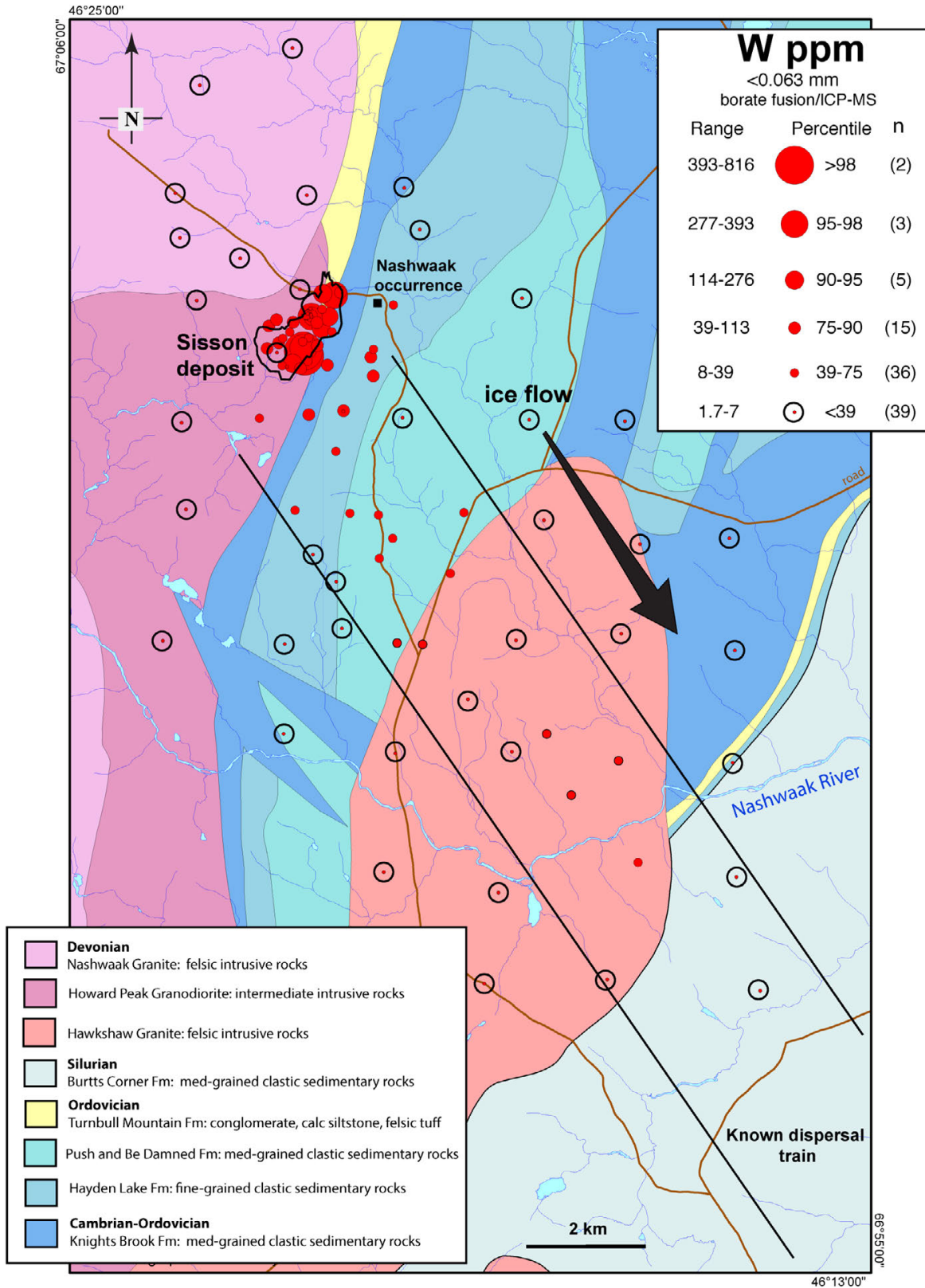


Figure 2 – Proportional dot map of W (borate fusion/ICP-MS) abundance in the <0.063 mm fraction of surface till samples around the Sisson W-Mo deposit. Known dispersal train outlined was identified using data from this study combined with that from Seaman and McCoy (2008). Bedrock geology modified from Smith and Fyffe (2006a, b, c, d). Deposit outline in black is from Rennie et al. (2013) (modified from McClenaghan et al., 2013c, 2014b).

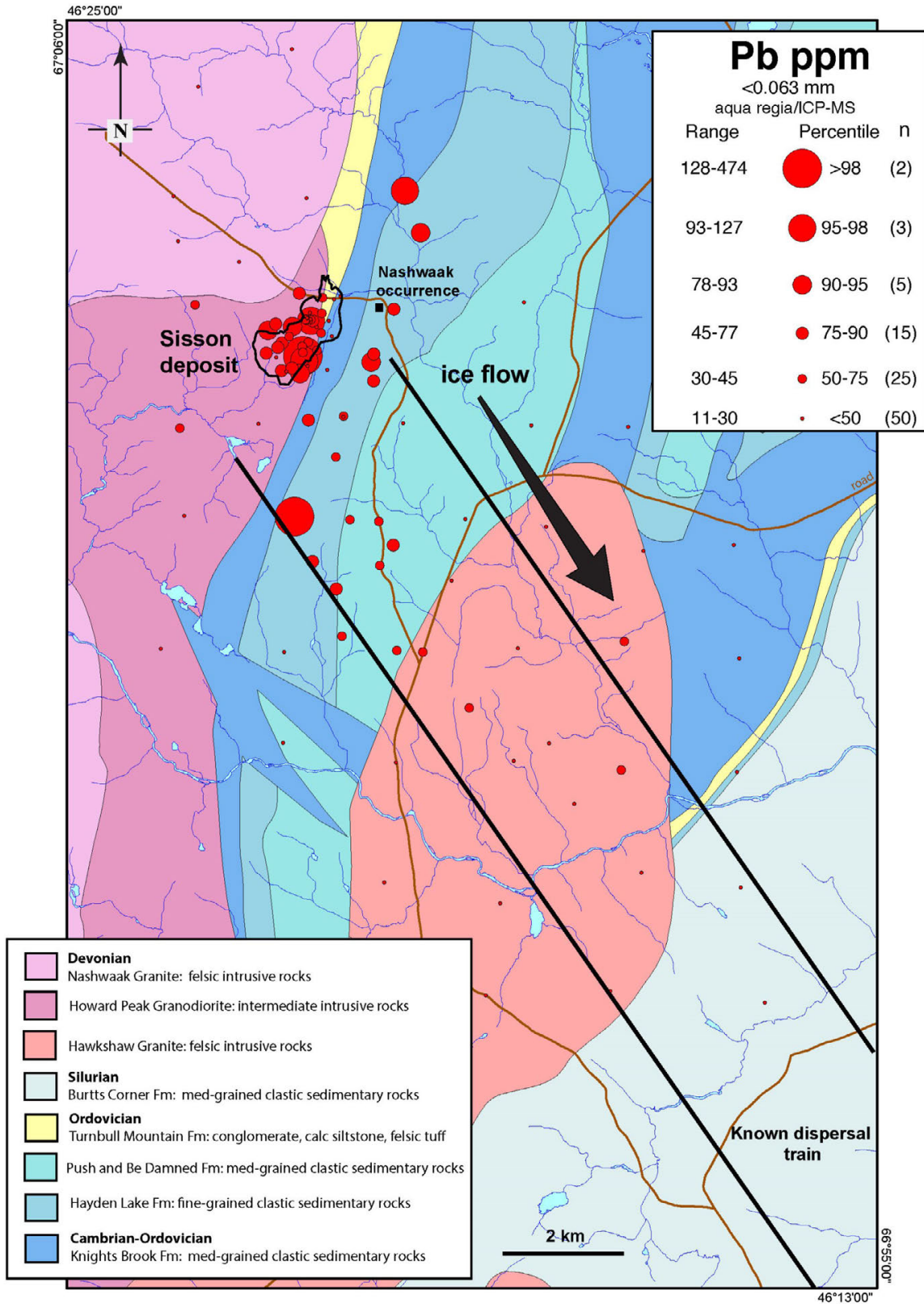


Figure 3 – Proportional dot map of Pb (modified aqua regia /ICP-MS) abundance in the <0.063 mm fraction of surface till samples around the Sisson W-Mo deposit. Bedrock geology modified from Smith and Fyffe (2006a, b, c, d). Deposit outline in black is from Rennie et al. (2013) (modified from McClenaghan et al., 2013c, 2014b).

Table 2 – Indicator minerals in the Sisson W-Mo deposit and those found in till heavy mineral concentrates (HMC) from the TGI-4 study (from McClenaghan et al., 2013a, b).

Mineral	Formula	Specific Gravity	Hardness	Presence in bedrock reported by others	Identified in bedrock PTS in this study	Identified in bedrock HMC in this study	Identified in till HMC in this study
W Minerals							
scheelite	CaWO ₄	5.9 - 6.1	4-5	Nast & Williams-Jones (1991); Marr (2009)	yes	yes	yes
wolframite	(Fe,Mn)WO ₄	7.1 - 7.5	4.5	Nast & Williams-Jones (1991); Marr (2009)	yes	yes	yes
Sulphides							
molybdenite	MoS ₂	5.5	1.0	Nast & Williams-Jones (1991); Marr (2009)	yes	yes	yes
pyrite	FeS ₂	5	6.5	Nast & Williams-Jones (1991); Marr (2009)	yes	yes	yes
chalcocopyrite	CuFeS ₂	4.1 - 4.3	3.5	Nast & Williams-Jones (1991); Marr (2009)	yes	yes	yes
sphalerite	(Zn,Fe)S	3.9 - 4.2	3.5-4	Nast & Williams-Jones (1991); Marr (2009)	yes	yes	yes
galena	PbS	7.2 - 7.6	2.5	Nast & Williams-Jones (1991); Marr (2009)	no	yes	yes
pyrrhotite	Fe _{(1-x)S} (x=0-0.17)	4.6 - 4.7	3.5-4	Nast & Williams-Jones (1991); Marr (2009)	yes	yes	no
arsenopyrite	FeAsS	6.1	5	Nast & Williams-Jones (1991); Marr (2009)	no	yes	yes
Bi Minerals							
bismuthinite	Bi ₂ S ₃	6.8 - 7.2	2.0	no	no	no	yes
bismutite	Bi ₂ (CO ₃)O ₂	7.0	4.0	no	no	no	yes
native bismuth	Bi	9.7 - 9.8	2-2.5	Nast & Williams-Jones (1991); Marr (2009)	yes	no	yes
joseite	Bi ₄ (S,Te) ₃	8.1	2.0	no	no	no	yes
Ag Minerals							
hessite	Ag ₂ Te	7.2-7.9	1.5-2	Nast & Williams-Jones (1991)	no	no	no
acanthite	Ag ₂ S	7.2-7.4	2-2.5	Nast & Williams-Jones (1991)	no	no	no

Mount Pleasant deposit geology

The bedrock geology of the Mount Pleasant deposit is summarized below from Kooiman et al. (1986), Invemo and Hutchinson, (2004), Sinclair et al. (2006), McCutcheon et al. (2010), and McCutcheon et al. (2013). The deposit is within two subvolcanic intrusions in the Late Devonian Mount Pleasant Caldera Complex along the north flank of the Saint George Batholith. The McDougall Brook Granitic Suite is related to the early stages of caldera development, and the Mount Pleasant Granitic Suite is related to the late stages of caldera development. The deposit consists of Sn, W, Mo, Bi, and In mineralisation that is genetically related to highly evolved granites of the Mount Pleasant Granitic Suite (Granites I, II and III) that are enriched in incompatible elements F, Li, Rb, Cs, U, Th, and Nb. Granite I and the related breccia hosts W-Mo-Bi mineralisation and Granite II hosts Sn-In mineralisation. Two mineralised zones outcrop or subcrop, the North Zone, and the Fire Tower Zone (Fig. 4), and thus likely contributed mineralised debris to overriding glaciers.

The North Zone consists of older W-Mo mineralisation and younger Sn-In mineralisation, some of which is at or near surface. The Sn-In zones contain cassiterite, arsenopyrite, loellingite, sphalerite, and chalcocopyrite as well as the other sulphide minerals listed in Table 3. The Fire Tower Zone contains predominantly large, low-grade W-Mo deposits with some small In-bearing Sn-base metal resources. The main ore minerals are wolframite and molybdenite and minor native bismuth, and bismuthinite. Gangue minerals include cassiterite, arsenopyrite, and loellingite, quartz, topaz, and fluorite. The Fire Tower Zone also contains small In-bearing Sn-base metal zones in irregular veins and breccias consisting mainly of cassiterite and wolframite along with the sulphide minerals listed in Table 3. Indium in the Mount Pleasant deposit occurs mainly as a solid solution between

sphalerite and roquesite, but also in chalcocopyrite and stannite (Sinclair et al., 2006).

Riddell (1967) was the first to describe the till geochemical signature of the Mount Pleasant deposit. He analysed over 2500 soils developed on till for Sn, Mo, Cu, Pb, and Zn. Metal contents are highest in soils overlying the North and Fire Tower Zones and to the southeast. Distribution patterns reflected glacial dispersal to the southeast from the two zones as well as subsequent mechanical dispersal and/or chemical dispersion of metals down the west and east flanks of the mountain. Szabo et al. (1975), building on the work of Riddell (1967), collected till samples instead of soil samples around the Mount Pleasant deposit. Glacial dispersal southeast from the deposit was best defined by Sn, As, Cu, Pb, and Zn in the 0.5-2.0 mm heavy mineral fraction (>2.95 specific gravity (SG)) of till.

Methods

Sampling

At both deposits, a small suite of mineralised and host rocks, and a larger suite of till samples were collected to examine their indicator mineral content. Till sampling locations, site descriptions, photographs, and sample depth information are reported in McClenaghan et al. (2013b, 2014a, b, 2015b). At each till sample site, three samples were collected: (1) a 8 to 15 kg sample for recovery of indicator minerals; (2) a 3 kg till sample for geochemical analysis of the matrix, textural determinations, and archiving; and, (3) a 200 g sample for in-field testing using a portable XRF. At the Sisson deposit, 61 surface till samples were collected from trenches, road cuts, and hand-dug holes around and within the first 14 km of the known glacial dispersal train to optimize the chances of sampling metal-rich till at varying

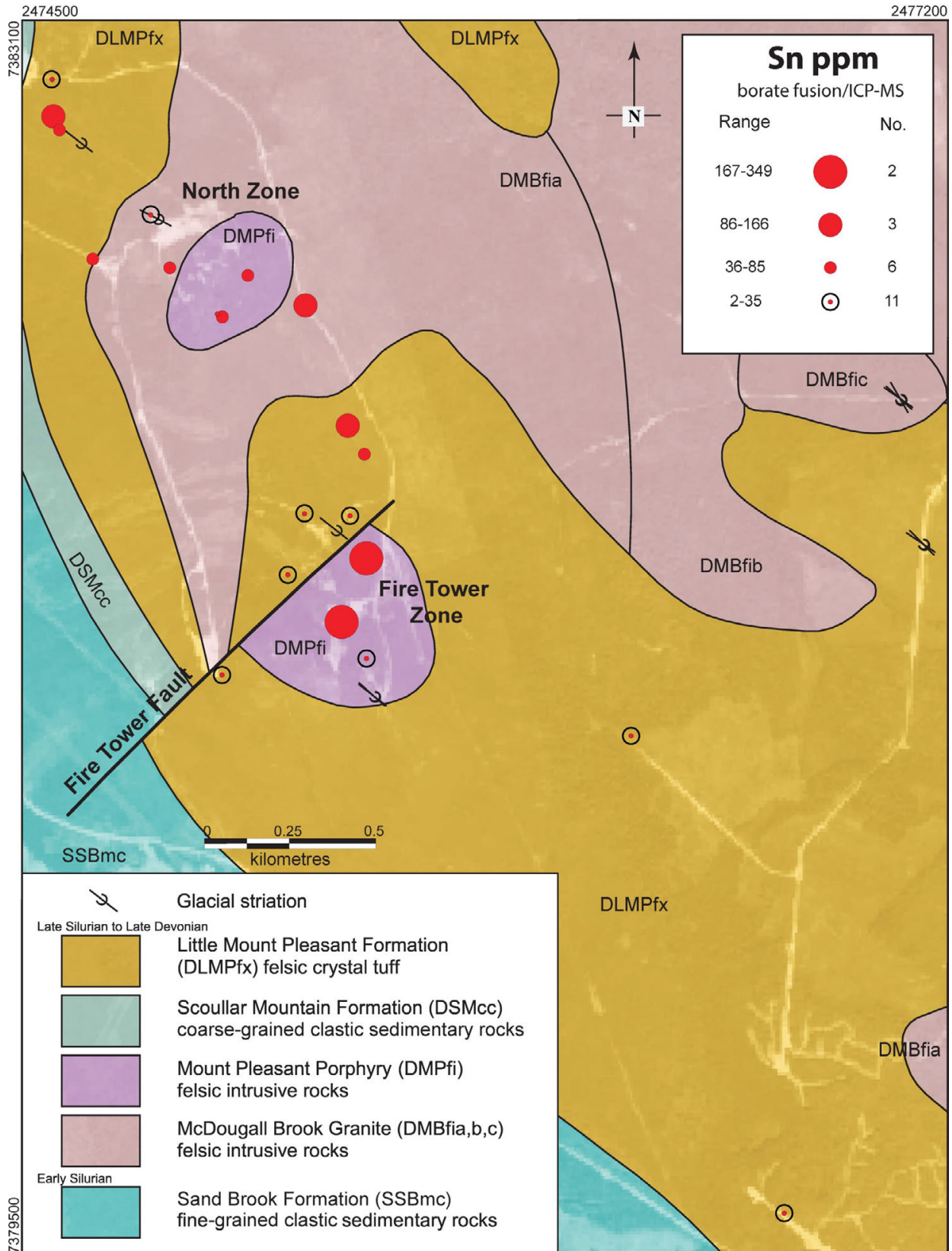


Figure 4 – Proportional dot map of Sn (borate fusion/ICP-MS) abundance in the <0.063 mm fraction of surface till samples around the Mount Pleasant Sn-W-Mo-Bi-In deposit. Bedrock geology from McLeod et al. (2005). (Modified from McClenaghan et al., 2015b).

Table 3 – Indicator minerals in the Mount Pleasant Sn-W-Mo-Bi-In deposit and those found in till heavy mineral concentrates (HMC) from the TGI-4 study (from McClenaghan et al., 2014a, 2015b).

Mineral	Formula	Hardness	Specific Gravity	Presence in bedrock reported by others	Size range in till HMC (mm)
Sn Minerals					
cassiterite	SnO ₂	6-7	6.8 - 7	Petruk (1972)	0.25-2.0
stannite	Cu ₂ FeSnS ₄	3.5-4	4.3 - 4.5	Petruk (1972)	not observed
k�sterite	Cu ₂ (Zn,Fe)SnS ₄	4.5	4.54 - 4.59	Petruk (1972)	not observed
ferrok�sterite	Cu ₂ (Fe,Zn)SnS ₄	4.0	4.5	Parrish (1977)	not observed
stannoidite	Cu ₈ Fe ₃ Sn ₂ S ₁₂	4	4.3	Petruk (1972)	not observed
mawsonite	Cu ₆ Fe ₂ SnS ₈	3.5-4	4.7	Petruk (1972)	not observed
W minerals					
scheelite	CaWO ₄	4-5	5.9 - 6.12	Parrish (1977)	0.25-2.0
wolframite	(Fe,Mn)WO ₄	4.5	7.1 - 7.5	Petruk (1972)	0.25-2.0
Sulphide and arsenide minerals					
molybdenite	MoS ₂	1.0	6	Petruk (1972)	0.25-0.5
pyrite	FeS ₂	6.5	5-5.02	Petruk (1972)	0.25-0.5
marcasite	FeS ₂	6.0-6.5	4.9	Petruk (1972)	not observed
sphalerite	(Zn,Fe)S	3.5-4	3.9 - 4.2	Petruk (1972)	not observed
pyrrhotite	Fe _(1-x) S (x=0-0.17)	3.5-4	4.58 - 4.65	Petruk (1972)	not observed
arsenopyrite	FeAsS	5	6.1	Petruk (1972)	0.25-2.0
loellingite	FeAs ₂	5.0	7.1 - 7.7	Petruk (1972)	0.25-1.0
ferrimolybdenite	Fe ₂ (MoO ₄) ₃ •8(H ₂ O)	2.5-3	4 - 4.5	Parrish (1977)	not observed
scorodite	Fe(AsO ₄)•2(H ₂ O)	3.5-4	3.1 - 3.3	Parrish (1977)	not observed
Bi minerals					
bismuthinite	Bi ₂ S ₃	2	6.8 - 7.2	Petruk (1972)	not observed
native bismuth	Bi	2-2.5	9.7 - 9.8	Petruk (1972)	not observed
arsenobismite	Bi ₂ (AsO ₄)(OH) ₃	3	5.7	Parrish (1977)	not observed
zairite	Bi(Fe,Al) ₃ (OH) ₆ (PO ₄) ₂]l	4.5	4.4	not reported	0.25-0.5
Cu minerals					
chalcocite	Cu ₂ S	2.5-3	5.5 - 5.8	Parrish (1977)	not observed
bornite	Cu ₅ FeS ₄	3.0	4.9 - 5.3	Petruk (1972)	not observed
chalcocite	Cu ₂ S	2.5-3	5.5 - 5.8	Parrish (1977)	not observed
roquesite	CuInS ₂	3.5-4	not reported	Petruk (1973)	not observed
digenite	Cu ₉ S ₅	2.5-3	5.6	Parrish (1977)	not observed
famatinite	Cu ₃ SbS ₄	3-4	4.6	Parrish (1977)	not observed
Pb minerals					
galena	PbS	2.5	7.2 - 7.6	Petruk (1972)	0.25-0.5
wittichenite	Cu ₃ BiS ₃	2.5	6.3 - 6.7	Petruk (1973)	not observed
galenobismutite	PbBi ₂ S ₄	2.5-3	6.9 - 7.1	Petruk (1972)	not observed
aikinite	PbCuBiS ₃	2-2.5	6.1 - 6.8	Petruk (1972)	not observed
cosalite	Pb ₂ Bi ₂ S ₅	2.5-3	6.4 - 6.8	Petruk (1972)	not observed
krupkaite	PbCuBi ₃ S ₆	4	7.0	Petruk (1972)	not observed
beudantite	PbFe ₃ (AsO ₄)(SO ₄)(OH) ₆	4.0	4.1-4.3	not reported	0.25-0.5
anglesite	Pb(SO ₄)	2.5-3	6.3	not reported	0.25-2.0
plumbogummite	PbAl ₃ (PO ₄) ₂ (OH) ₅ H ₂ O	4-5	4-5	not reported	0.25-0.5
plumboferrite	Pb ₂ Mn _{0.2} Mg _{0.1} Fe _{10.6} O _{18.4}	5	6	not reported	2.0
Au and Ag Minerals					
freibergite	(Ag,Cu,Fe) ₁₂ (Sb,As) ₄ S ₁₃	3.5-4	4.85 - 5	Petruk (1973)	not observed
pyrargyrite	Ag ₃ SbS ₃	2.5	5.9	Petruk (1973)	not observed
native silver	Ag	2.5-3	10-11	Petruk (1972)	not observed
gold	Au	2.5-3	16-19.3	Parrish (1977)	0.025-0.175
Alteration minerals					
topaz	Al ₂ SiO ₄ (F,OH) ₂	8	3.5 - 3.6	Petruk (1972)	0.25-2.0
fluorite	CaF ₂	4	3.01 - 3.25	Petruk (1972)	0.25-1.0
tourmaline (black)	NaAl ₃ Al ₆ (BO ₃) ₃ (Si ₆ O ₁₈)(O,OH) ₄	7	3	Petruk (1972)	0.25-1.0
columbite	(Fe,Mn)(Nb,Ta) ₂ O ₆	6.0	5.3 - 7.3	Petruk (1972)	not observed

distances down ice (Figs 2, 3). To provide a regional context in which to interpret the new till geochemical data for the Sisson area, the archived <0.063 mm fraction of 39 till samples, previously analysed by NBDEM as part of their regional surveys, were analysed as part of the GSC analytical batch in 2011 and data are reported in McClenaghan et al. (2013c). At the Mount Pleasant deposit, 18 surface till samples were collected from road cuts or hand-dug holes around the North and Fire Tower zones (Fig. 4) within the first 2 km of the known glacial dispersal train.

Stream sediment (silt + fine sand) and stream water samples were collected at 16 sites located upstream, overlying, and downstream (southeast) of the Sisson deposit using GSC National Geochemical Reconnaissance (NGR) sampling protocols (McClenaghan et al., 2015c). At each site, three samples were collected: (1) a 9 to 14 kg stream sediment sample for recovery of indicator minerals; (2) a 200 g fine grained (silt+fine sand) stream sediment sieved to <0.177 mm for geochemical analysis; and, (3) a 60 ml filtered (0.45 µm) stream water sample for geochemical analysis.

Geochemical analysis

The <0.063 mm (-250 mesh) fraction of till was geochemically analysed at a commercial laboratory (ACME Analytical Laboratories, Bureau Veritas Company, Vancouver, BC), using a modified aqua regia (HCl:HNO₃ 1:1) /ICP-MS on 0.5 g, and lithium metaborate/tetraborate fusion followed by nitric acid digestion/ICP-ES, ICP-MS on 0.2 g. As a result of the lower and variable recovery of W and Sn by the aqua regia digestion in this study (McClenaghan et al., 2013c), only the total W and Sn values determined by fusion/ICP-MS are described and plotted here. Detailed descriptions of analytical methods, monitoring of analytical accuracy and precision using blind duplicates, CANMET certified reference standards, and silica sand blanks along with the data listings are reported in McClenaghan et al. (2013b, c, 2015c).

The <0.177 mm (-80 mesh) fraction of stream sediment was geochemically analysed at a commercial laboratory using modified aqua regia/ICP-MS on 0.5 g and by Instrumental Neutron Activation Analysis (INAA) on ~30 g. Filtered stream water samples were acidified within 48 hours of arrival at GSC with 0.5 ml 8M HNO₃ and analysed for trace metal and major elements at GSC Laboratories, Ottawa. Detailed descriptions of analytical methods, monitoring of analytical accuracy and precision using blind duplicates and CANMET certified reference standards, and data listings for stream sediment and water samples are reported in McClenaghan et al. (2013b, 2015c).

Indicator mineral Analysis

All bedrock, till, and stream sediment samples were processed at the commercial heavy mineral processing laboratory, Overburden Drilling Management Limited (ODM) to recover the heavy mineral concentrate (HMC) and determine the abundance of indicator minerals in each sample. Prior to processing, bedrock samples were disaggregated using an electric pulse disaggregator instead of a conventional rock crusher to preserve natural grain sizes, textures, and shapes. The <2.0 mm fraction of each bedrock, till, and stream sediment sample was processed to produce a non-ferromagnetic HMC for selection of indicator minerals using the tabling and heavy liquid (3.2 SG) procedures outlined in McClenaghan et al. (2013a, b, 2014a, b, c, 2015a, c). The mid-density fraction mineral fraction (3.0-3.2 SG) was also separated for the Mount Pleasant till samples to allow for the determination of fluorite and tourmaline content. The 0.25-0.5, 0.5-1.0, and 1.0-

2.0 mm non-ferromagnetic HMC and the 0.25-0.5 mm mid density fractions of samples were then examined. Potential indicator minerals of Sn-W mineralisation were examined and counted and some grains removed for detailed study. In collaboration with ODM, a systematic method was developed to examine individual heavy mineral concentrates inside a black box using short wave ultraviolet light to rapidly and efficiently determine their scheelite content. Under visible light, scheelite has an unremarkable pale yellow colour, but under short wave ultraviolet light it has a diagnostic bright bluish white fluorescence.

Till geochemical results

The term 'indicator element' is used here to refer to an element that is an economically valuable component of the ore being sought and which may be used to detect an orebody. The term 'pathfinder element' refers to non-ore elements associated with the orebody that may be used to detect the orebody (Rose et al., 1979).

Sisson

Indicator elements for the Sisson deposit include W (Fig. 2) and Mo and pathfinder elements include Cu, Zn, Pb, Ag, Bi, In, As, Cd, Zn, and Te. This suite of elements is more extensive than the few elements (W, Mo, Cu, As, and F) identified in earlier studies by Snow and Coker (1987), Lamothe (1992), and Seaman and McCoy (2008). The <0.063 mm fraction of till sampled in this study clearly detects glacial dispersal at least 14 km to the southeast and confirms the observations of a southeast-trending glacial dispersal train reported in the earlier studies. Elevated concentrations of Ag, As, Cu, In, Pb (Fig. 3), Te, and Zn in till east and northeast of the Sisson deposit may reflect (1) glacial dispersal from a more distal expression of the Sisson mineralised system, such as the Nashwaak occurrence, or (2) glacial dispersal from metal-rich Silurian-Ordovician Tetagouche Group sedimentary rocks that are unrelated to the intrusion. These elevated metal concentrations may warrant further investigation to determine their bedrock source.

Mount Pleasant

Indicator elements for the Mount Pleasant deposit include Sn (Fig. 4), W, Mo, Bi, and In (Fig. 5). Pathfinder elements include Ag, As, Cd, Cu, Pb, Re, Te, Tl, and Zn. This suite of elements is significantly larger than (Sn, Mo, Cu, Pb, Zn) that identified by Riddell (1967) and Szabo et al. (1975) in their earlier geochemical studies of the deposit. The <0.063 mm fraction of till sampled in this study is metal-rich at least 1 km to the southeast and confirms the observations of a southeast-trending glacial dispersal train reported by Szabo et al. (1975). Samples 0.5 km to the northwest of the North Zone also have elevated contents of Sn, In, Ag, Cd, Zn, and Pb that likely reflect the presence of a small mineralised zone in this area. The Mount Pleasant deposit is a significant source of In and this study is one of the first to report In-rich till. Three till samples overlying the mineralised zones and one down-ice (southeast) of the North Zone contain 2.79 to 13.08 ppm In (Fig. 5), some of the highest In values ever reported for till.

Stream sediment and water geochemical results

Indicator/pathfinder elements in the <0.177 mm fraction of stream sediment downstream of the Sisson deposit include W, Mo, Ag, As, Bi, Cd, Cu, In, Tl, and Zn. Indicator/pathfinder elements in stream water around the Sisson deposit include W, Mo, As, Cd, Cu, Cs, and Zn (McClenaghan et al., 2015c).

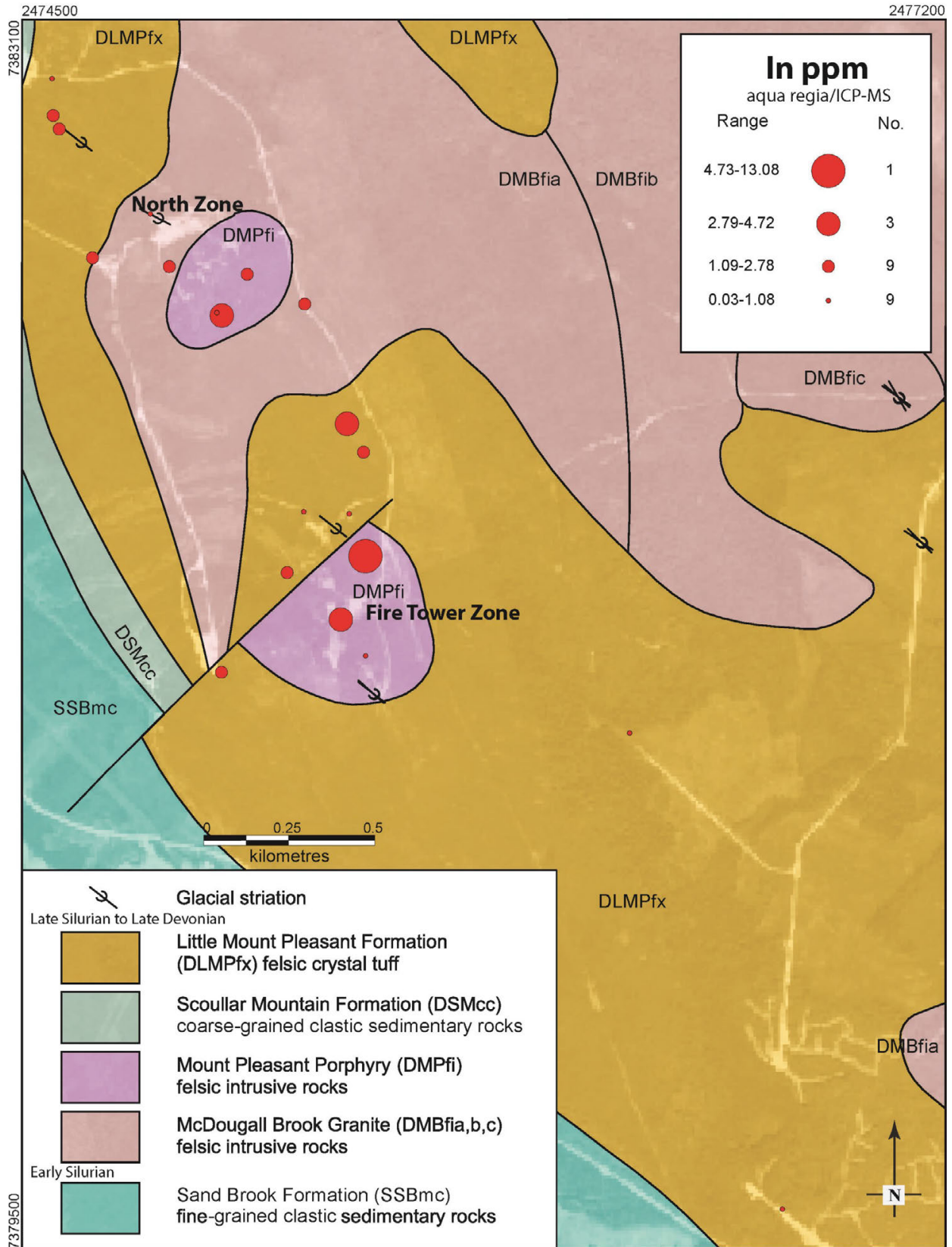


Figure 5 – Proportional dot map of In (modified aqua regia /ICP-MS) abundance in the <0.063 mm fraction of surface till samples around the Mount Pleasant Sn-W-Mo-Bi-In deposit. Bedrock geology from McLeod et al. (2005). (Modified from McClenaghan et al., 2015b).

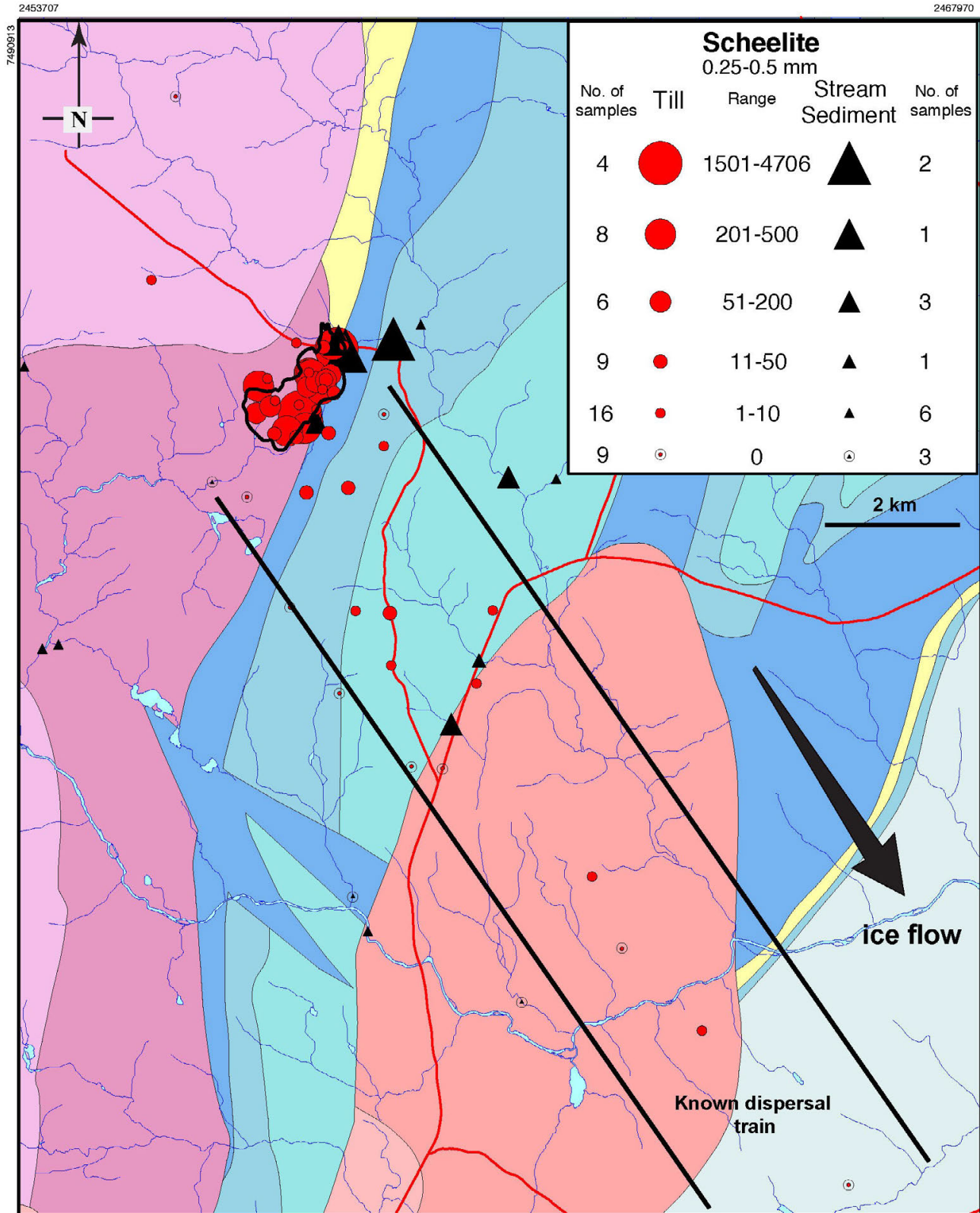


Figure 6 – Proportional symbol map of scheelite abundance in the 0.25-0.5 mm non-ferromagnetic fraction of surface till samples (red dots) and stream sediments (black triangles) around the Sisson W-Mo deposit. Bedrock geology modified from Smith and Fyffe (2006a, b, c, d). Deposit outline in black is from Rennie et al. (2013) (modified from McClenaghan et al., 2014a). Bedrock legend same as in Figure 3.

Indicator mineral results

Sisson

The primary Sisson ore minerals recovered from bedrock, till, and stream sediment samples include scheelite (Fig. 6), wolframite, and molybdenite (Table 2). They are heavy minerals that are visually distinct (Fig. 7) and easily recovered by the common surficial sample processing method that uses tabling + heavy liquids (McClenaghan, 2011). Additional indicator minerals include chalcopyrite, Bi-rich minerals (joseite, native Bi, bismutite, bismuthinite), galena, sphalerite, arsenopyrite, spessartine, pyrrhotite, and pyrite. These minerals

are most abundant in the 0.25-0.5 mm fraction of till. Coarse (0.5-2.0 mm) indicator minerals are present in till up to 4 km down ice of the deposit.

Mount Pleasant

Indicator minerals in bedrock and till at the Mount Pleasant deposit (Table 3) include the main ore minerals, cassiterite (Fig. 8), wolframite, and molybdenite, as well as topaz, galena, sphalerite, chalcopyrite, galena, arsenopyrite, pyrrhotite, pyrite, and loellingite in the >3.2 SG fraction of till, and fluorite in the 3.0-3.2 SG fraction (Fig. 9). Useful indicator minerals also include secondary Pb sulphate minerals

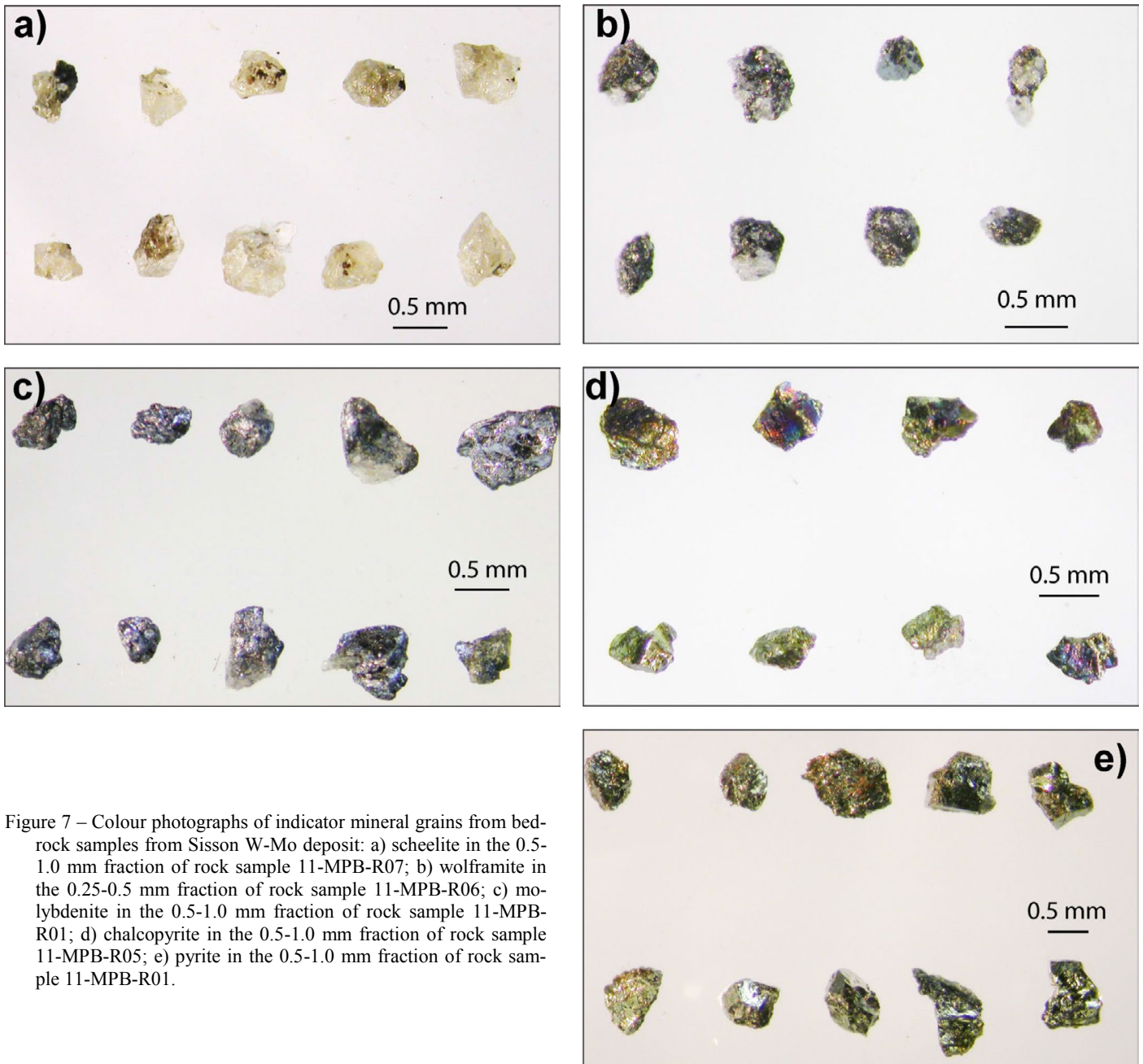


Figure 7 – Colour photographs of indicator mineral grains from bedrock samples from Sisson W-Mo deposit: a) scheelite in the 0.5-1.0 mm fraction of rock sample 11-MPB-R07; b) wolframite in the 0.25-0.5 mm fraction of rock sample 11-MPB-R06; c) molybdenite in the 0.5-1.0 mm fraction of rock sample 11-MPB-R01; d) chalcopyrite in the 0.5-1.0 mm fraction of rock sample 11-MPB-R05; e) pyrite in the 0.5-1.0 mm fraction of rock sample 11-MPB-R01.

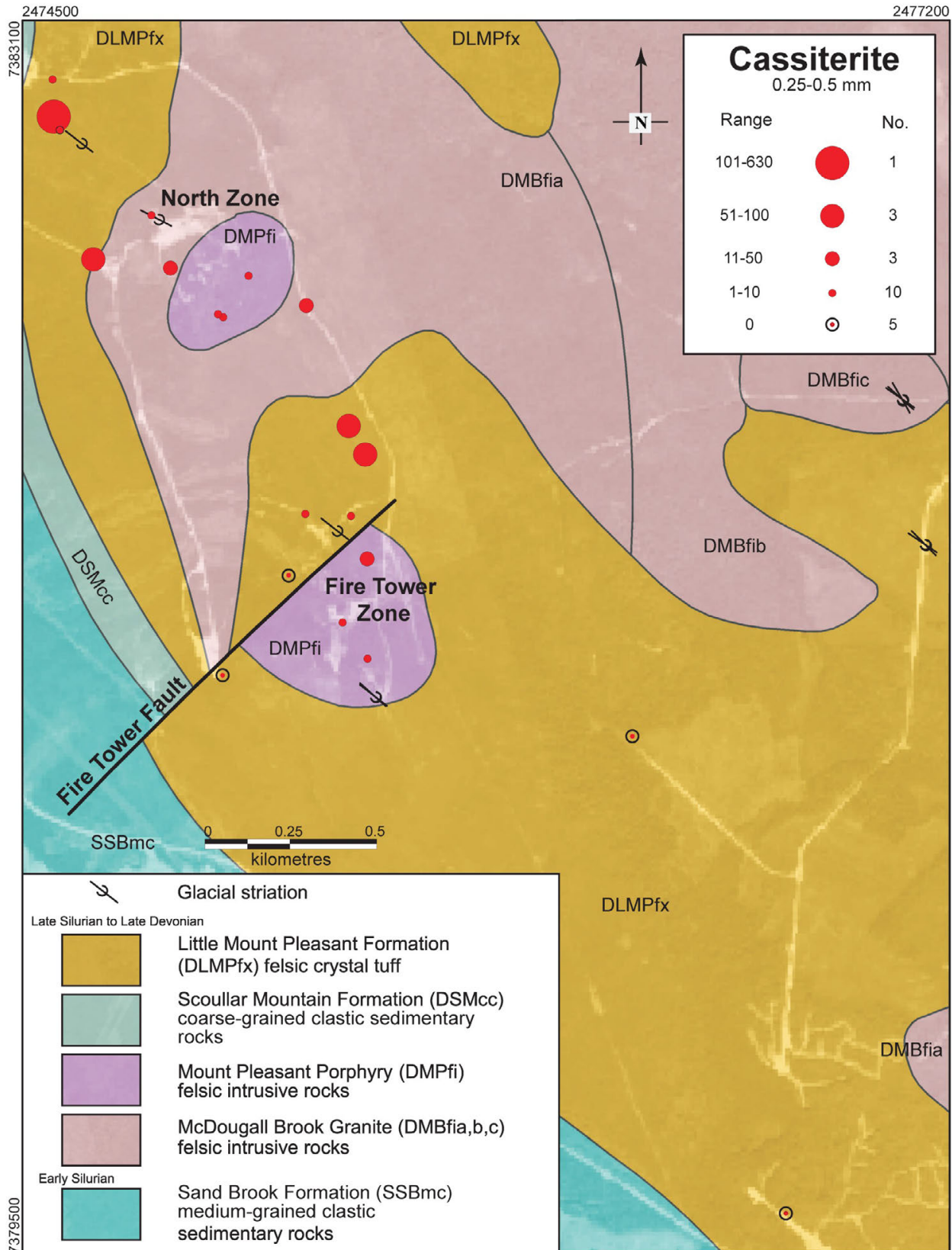


Figure 8 – Proportional dot map of cassiterite abundance in the 0.25-0.5 mm non-ferromagnetic fraction of surface till samples around the Mount Pleasant Sn-W-Mo-Bi-In deposit. Bedrock geology from McLeod et al. (2005).

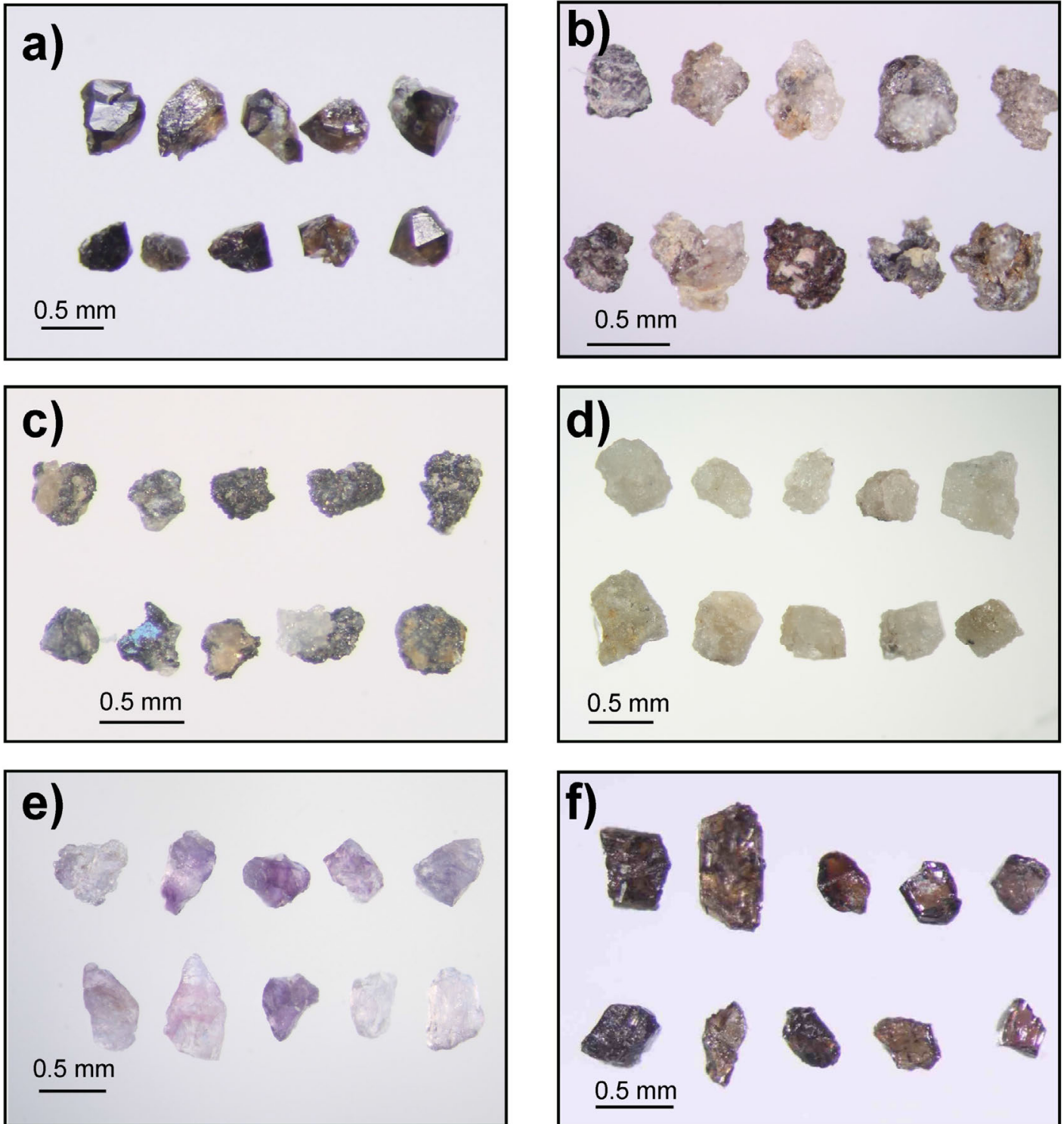


Figure 9 – Colour photographs of indicator mineral grains from till in the Mount Pleasant deposit area: a) prismatic brown cassiterite grains in the 0.25-0.5 mm fraction of sample 12-MPB-1020; b) brown irregular shaped cassiterite grains with adhering quartz in the 0.25-0.5 mm fraction of sample 12-MPB-1020; c) wolframite in the 0.25-0.5 mm fraction of sample 12-MPB-1004; d) topaz in the 0.5-1.0 mm fraction of sample 12-MPB-1004; and e) fluorite in the 0.5-1.0 mm fraction of 12-MPB-1008; f) tourmaline in the 0.25-0.5 mm fraction of sample 12-MPB-1007; g) beudantite in the 0.25-0.5 mm fraction of sample 12-MPB-1002; h) anglesite in the 0.25-0.5 mm fraction of sample 12-MPB-1004; i) eulytite in the 0.25-0.5 mm fraction of 12-MPB-1002; j) ziarite in the 0.25-0.5 mm fraction of 12-MPB-1019. Photographs taken by Overburden Drilling Management Ltd.

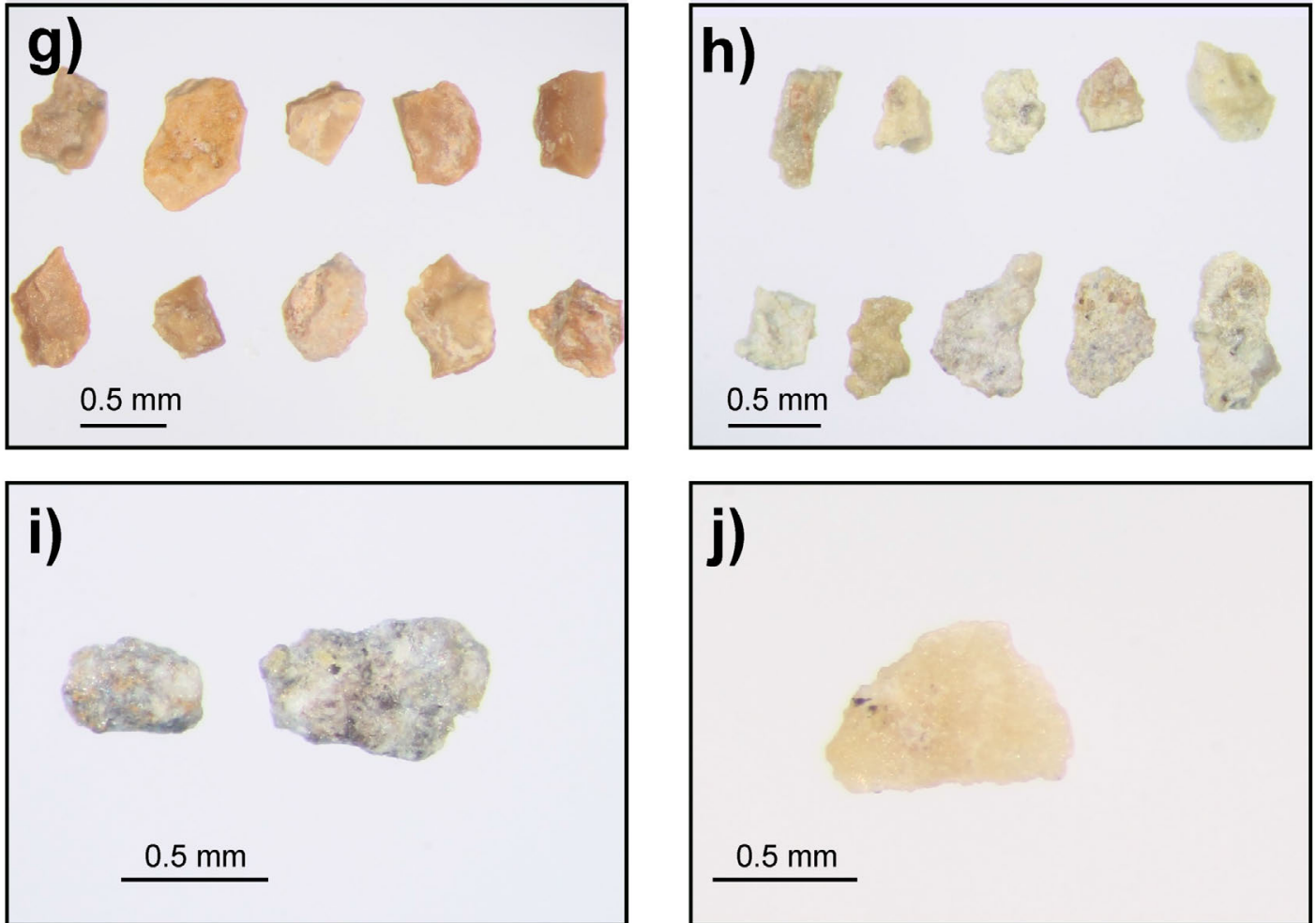


Figure 9 – Continued

beudantite ($\text{PbFe}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$) and anglesite ($\text{Pb}(\text{SO}_4)$) and the Pb phosphate mineral plumbogummite ($\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5\text{H}_2\text{O}$), which formed from the oxidation and weathering of galena (Fig. 9). Samples 0.5 km to the northwest of the North Zone also have elevated contents of cassiterite, tourmaline, pyrite and anglesite that likely reflect the presence of a small mineralised zone in this area. Collectively, the indicator minerals identified in this study reflect the presence of Sn mineralisation as well as the polymetallic nature of the deposit. These minerals are most abundant in the 0.25-0.5 mm fraction of till. Coarse (0.5-2.0 mm) indicator minerals are present in till within <1 km down ice of each zone.

Scheelite mineral chemistry

Scheelite (CaWO_4) varies from a common to an accessory phase in a variety of hydrothermal ore-deposit settings, including Cu-Mo-W porphyry systems, skarns and vein Sn-W. Scheelite is an economically important source of W, but can also, by association, be an important indicator of ore minerals in other deposit types, such as Au systems (De Smeth, 1985; Robert and Brown, 1986). Because scheelite is a common indicator mineral in surficial sediments (Averill, 2001;

Horsnail, 1979; Hosking 1982; Ottensen and Theobald, 1994), a detailed study of scheelite grains from 37 deposits was carried out as part of this TGI 4 study to determine if chemistry of scheelite grains in surficial sediments could be used to identify their ore-deposit setting. This research was carried out at Laurentian University, Sudbury as a M.Sc. thesis supported by the GSC's Research Affiliate Program (RAP). Preliminary results have been reported in numerous conference abstracts, posters, and talks (Poulin et al., 2013a, b, 2014a, b). A variety of analytical methods were used to fully characterize and develop a chemical database (e.g., trace elements, stable isotope ($\delta^{18}\text{O}$), cathodoluminescence). Results indicate that scheelite is a chemically complex mineral exhibiting large ranges in the investigated parameters, including: (1) zonation, varying from absent to normal, oscillatory and discordant; (2) minor-element composition, in particular highly variable As and Mo concentrations; (3) trace-element chemistry, specifically the REEs which vary in terms of ΣREEs , degree and type of fractionation pattern observed (flat, convex, concave), and type and magnitude of the Eu anomalies (positive or negative); and (4) isotope chemistry, specifically $\delta^{18}\text{O}$ ranging from -4.6 to +9.1‰.

Discussion

Till geochemistry

Most reports describing the use of till geochemistry for Sn and W exploration were published between the 1970s and early 1990s. The analytical methods used for Sn and W in these studies were highly specialized, required a separate and unique method just to determine W or Sn, and added to the cost of routine analytical methods used for other elements. Lithium meta/tetraborate fusion ICP-MS is now routinely used to determine the total concentration of Sn and W in sediments and is a fast and cost effective method.

The extensive suites of indicator/pathfinder trace elements in till and stream sediments at Sisson, and in till at Mount Pleasant, reflect the polymetallic nature of the deposits as well as the ability of modern ICP-MS techniques to determine a broad suite of elements at low detection limits. The indicator/pathfinder element suites are more extensive than previously reported in published till studies around other Sn-W mineralisation (e.g. Steiger, 1977; Matilla and Peuraniemi, 1980; Toverud, 1984; Peuraniemi et al., 1984; Johansson et al., 1986; Coker et al., 1988; Rogers et al., 1990).

Indicator mineral results

Most reports describing the use of indicator minerals for Sn and W exploration were published between the 1970s and early 1990s and

were focused on the recovery of scheelite, wolframite, and cassiterite (e.g. Brundin and Bergström, 1977; Ottensen & Theobald, 1994). The heavy mineral recovery methods used in these older studies were highly specialized, specific to each study, not readily available in commercial laboratories, and applied only after a Sn or W-rich samples was geochemically identified.

The extensive list of indicator minerals in till and stream sediments at Sisson and in till at Mount Pleasant, reflect the polymetallic nature of the deposits as well as the ability of modern indicator mineral methods to recover and recognize a broad range of minerals. The indicator minerals identified in these new studies are more extensive than previously published till studies around Sn-W mineralisation (e.g. Szabo et al. 1975; Brundin & Bergstrom 1977; Matilla and Peuraniemi, 1980; Toverud, 1984; Snow and Coker, 1987; Friske et al., 2001).

Recovery of this broad list of indicator minerals is now consistent, routine and fast. The advantages of indicator mineral methods over traditional geochemical analysis of the heavy mineral or the <0.063 mm fraction are that the mineral grains: (1) are visible and can be examined; (2) provide physical evidence of the presence of mineralisation or alteration; (3) provide information about the source that traditional geochemical methods cannot, including nature of the ore, alteration, and proximity to source; (4) equivalent of ppb detection levels when there are just a few grains (Brundin and Bergstrom, 1977; Averill, 2001).

Table 4 – List of indicator mineral short course and workshop presentations given as part of the TGI-4 intrusion-hosted Sn-W research project.

Workshop/Short Course	Date	Topic
Laurentian University, Modular Course in Exploration Geochemistry	December, 2010	Indicator mineral and till geochemical methods for mineral exploration
Association of Applied Geochemists Short Course: Indicator Mineral Methods in Mineral Exploration	August 21, 2011	Modern techniques for the recovery of indicator minerals from surficial sediments
PDAC Student-Industry Mineral Exploration Workshop (S-IMEW)	May 11, 2012	Indicator mineral and till geochemical methods for mineral exploration
Laurentian University, Modular Course in Exploration Geochemistry	December 2012	Modern techniques for the recovery of indicator minerals from surficial sediments
Association for Mineral Exploration British Columbia Short Course: Exploring Through Cover - What Works, What Doesn't & Why	January 26, 2013	Modern techniques for the recovery of indicator minerals from surficial sediments
PDAC Workshop: New Frontiers for Exploration in Glaciated Terrain	March 1, 2013	Quality assurance and quality control measures for indicator mineral programs
PDAC Student-Industry Mineral Exploration Workshop (S-IMEW)	May 10, 2013	Modern techniques for the recovery of indicator minerals from surficial sediments
Geological Survey of Finland, Green Mining Project Workshop	September 11, 2013	Application of indicator mineral methods to mineral exploration in Canada
Association of Applied Geochemists Short Course: Application of Indicator Mineral Methods to Mineral Exploration	November 17, 2013	Modern analytical techniques for indicator mineral chemistry
Association of Applied Geochemists Short Course: Application of Indicator Mineral Methods to Mineral Exploration	November 17, 2013	Indicator mineral methods for intrusion-hosted W-Mo deposits, with examples from the Sisson deposit
Association for Mineral Exploration British Columbia Short Course: Surficial Geology and Exploration Geochemistry – Know What You Are Sampling & Why	January 24, 2014	Modern techniques for the recovery of indicator minerals from surficial sediments
PDAC Student-Industry Mineral Exploration Workshop (S-IMEW)	May 7, 2014	Modern techniques for the recovery of indicator minerals from surficial sediments
Canadian Institute of Mining and Metallurgy Short Course: Prospecting Under Cover	November 5, 2014	Modern techniques for the recovery of indicator minerals from surficial sediments
Laurentian University, Modular Course in Exploration Geochemistry	December, 2014	Modern techniques for the recovery of indicator minerals from surficial sediments

Comparison of indicator minerals and till geochemistry

In this study, not all till samples that contain cassiterite have corresponding high Sn values in the <0.063 mm fraction. Not all till or stream sediment samples that contain scheelite or wolframite, have high W values. Conversely, samples with elevated Sn or W contents always contain indicator minerals. These patterns suggest that indicator minerals can be more effective than till and/or stream sediment geochemistry for identifying the presence of Sn and W mineralisation.

At Mount Pleasant, Cu, Pb, Zn, Ag, As, and In values are high for many of the till samples, however ore-associated sulphide mineral (e.g. galena, sphalerite, chalcocopyrite, arsenopyrite) abundance in the same till samples is low to zero. Pb-bearing secondary minerals beudantite, anglesite, and plumbogummite are present in these same till samples. These patterns indicate that sulphide minerals were either destroyed during pre- or post-glacial oxidation, or both. As a result, till geochemistry and the presence of secondary sulphate or phosphate minerals are useful for identifying the presence and polymetallic (Cu, Pb, Zn, Ag, As, and In) metal-rich debris glacially eroded from the deposit.

Technology transfer

Education and dissemination of information about the application of indicator mineral methods to mineral exploration have been a particular focus of this TGI 4 research activity, with special emphasis on intrusion-hosted Sn-W-Mo exploration. In addition to the publications listed in Table 1, overviews of indicator mineral methods and TGI 4 research results have been presented at numerous workshops and short courses listed in Table 4.

Conclusions and implications for exploration

- The till geochemical + mineralogical studies reported here are among the first detailed studies around major Sn-W deposits in glaciated terrain.
- A broad suite of indicator/pathfinder trace elements for both deposits was identified (Table 5) and these reflect the polymetallic nature of these Sn-W-Mo deposits and the broader suite of elements that is now available using modern ICP-MS techniques. In both case studies, the list of indicator/pathfinder elements is more extensive than previously identified in published soil and till geochemical studies of Sn-W deposits in glaciated terrain.

- The <0.063 mm fraction of till reflects glacial dispersal from both deposits, therefore, use of this till size fraction in regional exploration programs for intrusion-hosted Sn-W-Mo deposits is recommended.
- The Mount Pleasant deposit is a significant source of indium and till down ice of the deposit contains some of the highest indium values ever published for till, indicating that till geochemistry can be an important exploration tool for detecting In-bearing deposits.
- The study compared the efficiency of a modified aqua regia leach versus a lithium metaborate/tetraborate fusion followed by nitric acid digestion (total digestion) for determining metal contents in till. Results indicate that a total digestion is required to report the total concentration of Sn and W in till. The modified aqua regia leach is suitable for determining the other indicator and pathfinder elements.
- Our study identified an area of elevated metal content in till east and northeast of the Sisson deposit overlying Ordovician rocks that warrants further investigation. The bedrock source of the elevated metal contents may be related to a small polymetallic occurrence east of the Sisson deposit or other unknown metal-rich rocks in the area.
- Indicator minerals identified in the 0.25-0.5 mm fraction of mineralised bedrock, till, and stream sediments include a suite of Sn- and W- bearing minerals as well as sulphide, arsenide, telluride, and alteration minerals (Table 5). Additional but rare indicator minerals include beudantite, anglesite, and plumbogummite which formed by oxidation and weathering of the galena. The extensive suite of indicator minerals reflects the polymetallic nature of the deposits and the ability of modern indicator mineral methods to recover these minerals.
- Indicator minerals are also present in the coarse (0.5-2.0 mm) HMC fraction of till samples that are proximal to the deposits, and thus indicator mineral size can provide some insights into glacial transport distance and proximity to the bedrock source.
- Under short wave ultraviolet light, scheelite has a diagnostic bright bluish white fluorescence. A systematic method to rapidly and efficiently determine the scheelite content of heavy mineral concentrate using this fluorescence has been developed and is now commercially available from the laboratory Overburden Drilling

Table 5 – Summary of indicator+pathfinder trace elements in till, stream sediments and stream water, and indicator minerals in bedrock, till and stream sediments at the Sisson W-Mo and Mount Pleasant Sn-W-M-Bi-In deposits.

Deposit	Deposit elements	Media	Indicator/ Pathfinder elements	Indicator Minerals
Sisson	W-Mo	till	W, Mo, Cu, Zn, Pb, Ag, Bi, In, As, Cd, Zn, Te	scheelite, wolframite, molybdenite, chalcocopyrite, joseite, native Bi, bismutite, bismuthinite, galena, sphalerite, arsenopyrite, pyrrhotite, pyrite
		bedrock	<i>not determined</i>	scheelite, wolframite, molybdenite, chalcocopyrite, sphalerite, galena, pyrite, native bismuth
		stream sediment	W, Mo, Ag, As, Bi, Cd, In, Tl, Cu, Zn	scheelite, wolframite, molybdenite, chalcocopyrite, sphalerite, arsenopyrite, pyrite
		stream water	W, Mo, As, Cd, Cu, Cs, Zn	
Mount Pleasant	Sn-W-Mo-Bi-In	till	Sn, W, Mo, Bi, In, Ag, As, Cd, Cu, Pb, Re, Te, Tl, Zn	cassiterite, wolframite, molybdenite, topaz, galena, arsenopyrite, loellingite, fluorite, beudantite, anglesite, plumbogummite
		bedrock	<i>not determined</i>	cassiterite, molybdenite, sphalerite, chalcocopyrite, pyrite, galena, arsenopyrite, fluorite, topaz

Management Limited. This method will provide consistent and comparable scheelite counts for till and stream sediment samples within and between projects.

- Fluorite abundance is greatest in the 3.0-3.2 SG mid-density fraction of till as compared to the >3.2 SG heavy fraction. Thus, when exploring for deposits for which fluorite is an indicator mineral, the mid-density fraction of till should be examined.

Future research

Future studies on the mineral chemistry of scheelite and other physically and chemically robust minerals identified as part of this study (e.g. cassiterite) should be pursued. New indicator mineral recovery and chemical characterization methods are currently being developed to reduce sample size and analytical costs. Ongoing and future research will focus on smaller size fractions of till that currently are not examined (i.e., <0.063 mm) and the applications of new and more accessible analytical instruments to indicator mineral studies (i.e., hyperspectral, mineral liberation analysis (MLA) express) (Layton-Matthews et al., 2014). These developments will ultimately lead to the identification of new and/or improved indicator mineral methods of intrusion-hosted deposits and increased mineral exploration effectiveness.

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