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Indicator mineral and geochemical signatures associated with the Sisson W–Mo deposit, New Brunswick, Canada

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Abstract: An indicator mineral and geochemical case study was carried out around the Sisson W–Mo deposit to test modern indicator mineral and analytical methods and document glacial and fluvial dispersal from a significant W–Mo source. Indicator minerals in the 0.25 – 2.0 mm non-ferromagnetic heavy mineral fraction of till and stream sediments include the primary ore minerals scheelite, wolframite and molybdenite, as well as chalcopyrite, joseite, native Bi, bismutite, bismuthinite, galena, sphalerite, arsenopyrite, pyrrhotite and pyrite. Indicator minerals in *c.* 12 – 14 kg samples define glacial dispersal of at least 10 km down ice (SE) of the deposit and fluvial dispersal at least 4 km downstream. The presence of very coarse (0.5 – 2.0 mm) indicator minerals in till and stream sediments marks proximity (<1 km) to the mineralized source. Indicator elements for the deposit in the <0.063 mm fraction of till, the <0.177 mm fraction of stream sediments, and in stream water include W and Mo, and various combinations of pathfinder elements Ag, As, Bi, Cd, Cu, In, Pb, Te and Zn. This list of elements is more extensive than previously identified for the Sisson deposit or other studies around W mineralization in glaciated terrain. The study demonstrates that indicator mineral methods, so well known for diamond and gold exploration, have a broader application that includes W–Mo exploration.

Keywords: indicator minerals; till geochemistry; scheelite; molybdenite; stream sediments

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The use of till geochemistry for W–Mo exploration in glaciated terrain is well documented from case studies and exploration programs carried out in the 1970s to 1990s (Nikkarinen & Björklund 1976; Salminen & Hartikainen 1986; Snow & Coker 1987; Coker *et al.* 1988; Rogers *et al.* 1990). In some of this earlier work, the heavy mineral fraction of till was analyzed geochemically to determine its W content as a proxy for the presence of the most common W-bearing mineral, scheelite (Brundin & Bergström 1977; Toverud 1984; Coker *et al.* 1988). In some cases, samples with anomalous W values were subsequently examined to confirm the presence of scheelite (Stea & O'Reilly 1982; Ryan *et al.* 1988; Peuraniemi 1992). In other studies, heavy mineral concentrates were systematically examined to detect the presence of scheelite (Lindmark 1977; Toverud 1984; Johansson *et al.* 1986; Petersen & Stendal 1987; Peuraniemi 1987; Aario & Peuraniemi 1992). Scheelite is relatively easy to visually identify because it fluoresces under shortwave ultraviolet light. Results from these early heavy mineral studies are difficult to compare because of the inadequate reporting of heavy mineral processing methodologies, the variation in concentration methods used, and the variation in size fractions examined. None of these studies utilized the systematic indicator mineral recovery and grain counting methods that are now commercially available to the exploration industry (McClenaghan 2011; Plouffe *et al.* 2013; Averill 2017).

The undeveloped Sisson W–Mo deposit in eastern Canada was used to test and demonstrate modern and systematic heavy mineral methods for exploration for intrusion-hosted W–Mo deposits. This deposit was chosen because: (1) the bedrock and surficial geology are well documented; (2) it was exposed to glacial erosion and is now till-covered; and (3) till and stream sediment geochemical signatures of the deposit have been reported by others and thus metal-rich till and stream sediments should be available for sampling in this study.

This indicator mineral study was carried out as part of the Geological Survey of Canada's (GSC) Targeted Geoscience Initiative 4 (TGI-4), a federal geoscience program with a mandate to provide industry with the next generation of geoscience knowledge and innovative techniques for more effective targeting of buried mineral deposits. The study is a collaborative effort between the GSC, the New Brunswick Department of Energy and Resource Development (NBDERD), Northcliff Resources Ltd, Hunter Dickinson Inc., and Laurentian University. This paper provides an overview of the mineralogical and geochemical signatures in till and stream sediments around the deposit.

Location and access

The Sisson deposit is in the eastern Canadian province of New Brunswick (Fig. 1) at latitude 46°22′01″ N and longitude 67°03′00″ W in the Coldstream map area (NTS 21 J/06). It is located 60 km NW of the city of Fredericton and is easily accessed by logging roads.

Bedrock geology

The bedrock geology of the Sisson deposit area is summarized below from Nast & Williams-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

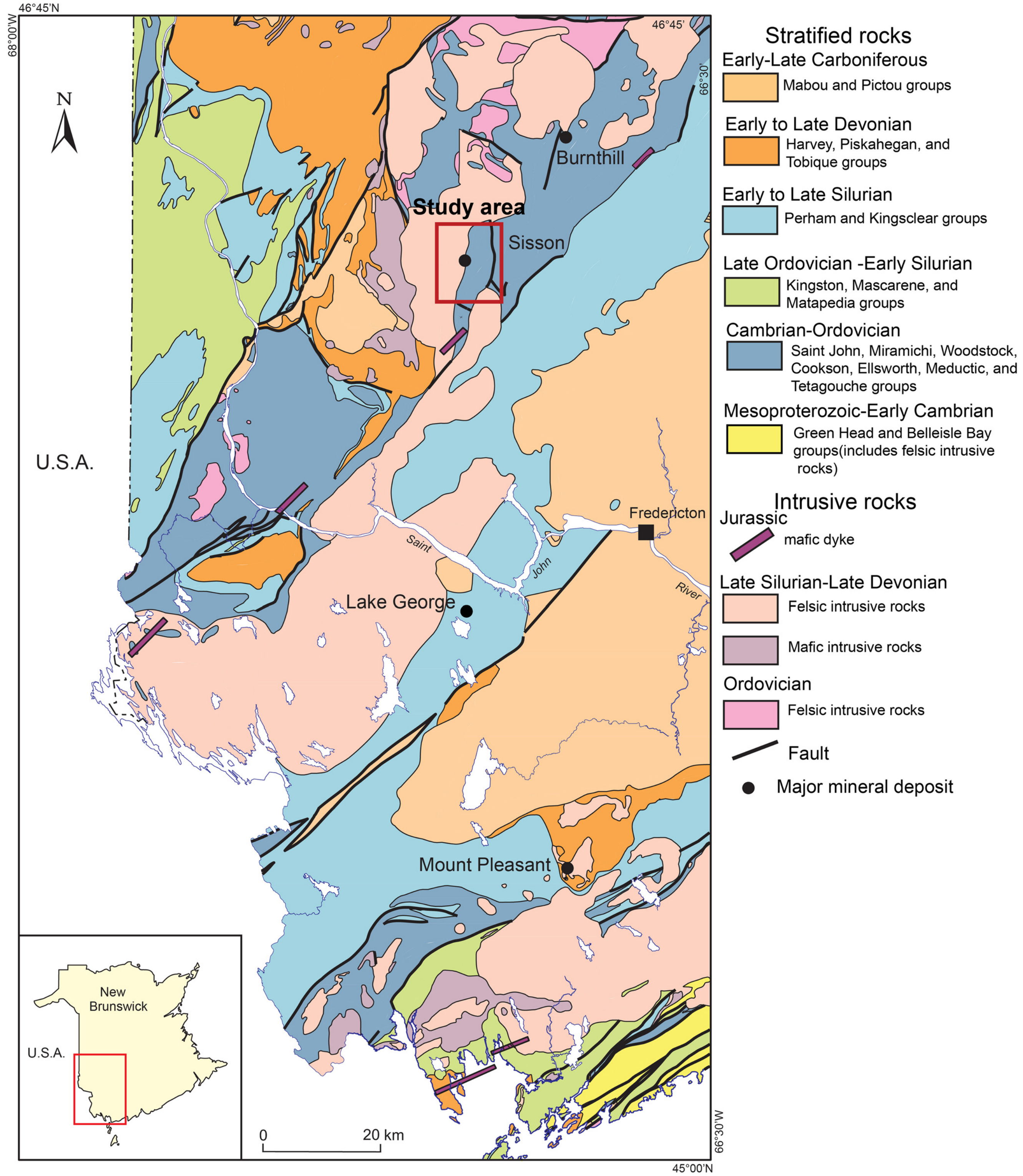

Fig. 1. Bedrock geology of west-central and southern New Brunswick showing the location of the Sisson W–Mo deposit and other significant intrusion-hosted deposits (modified from Fyffe *et al.* 2010).

Granite and Howard Peak Granodiorite plutons (Fig. 2) with Ordovician volcanic and sedimentary rocks and Cambro-Ordovician sedimentary rocks to the east. 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 mineralization that straddle the strongly sheared eastern contact of the Howard Peak Granodiorite. Mineralization 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. Rennie *et al.* (2013) reported resource estimates for the deposit of 383 Mt at 0.069% WO_3 and 0.023% Mo (proven) and 178 Mt at 0.065 WO_3 and 0.020% Mo (probable), making it one of the largest W deposits in the world. Ore minerals in the deposit include scheelite, molybdenite and minor wolframite. Potential indicator minerals present in the deposit are listed in Table 1.

East of the Howard Peak Granodiorite are Ordovician tuffaceous volcanic and sedimentary rocks of the Turnbull Mountain Formation

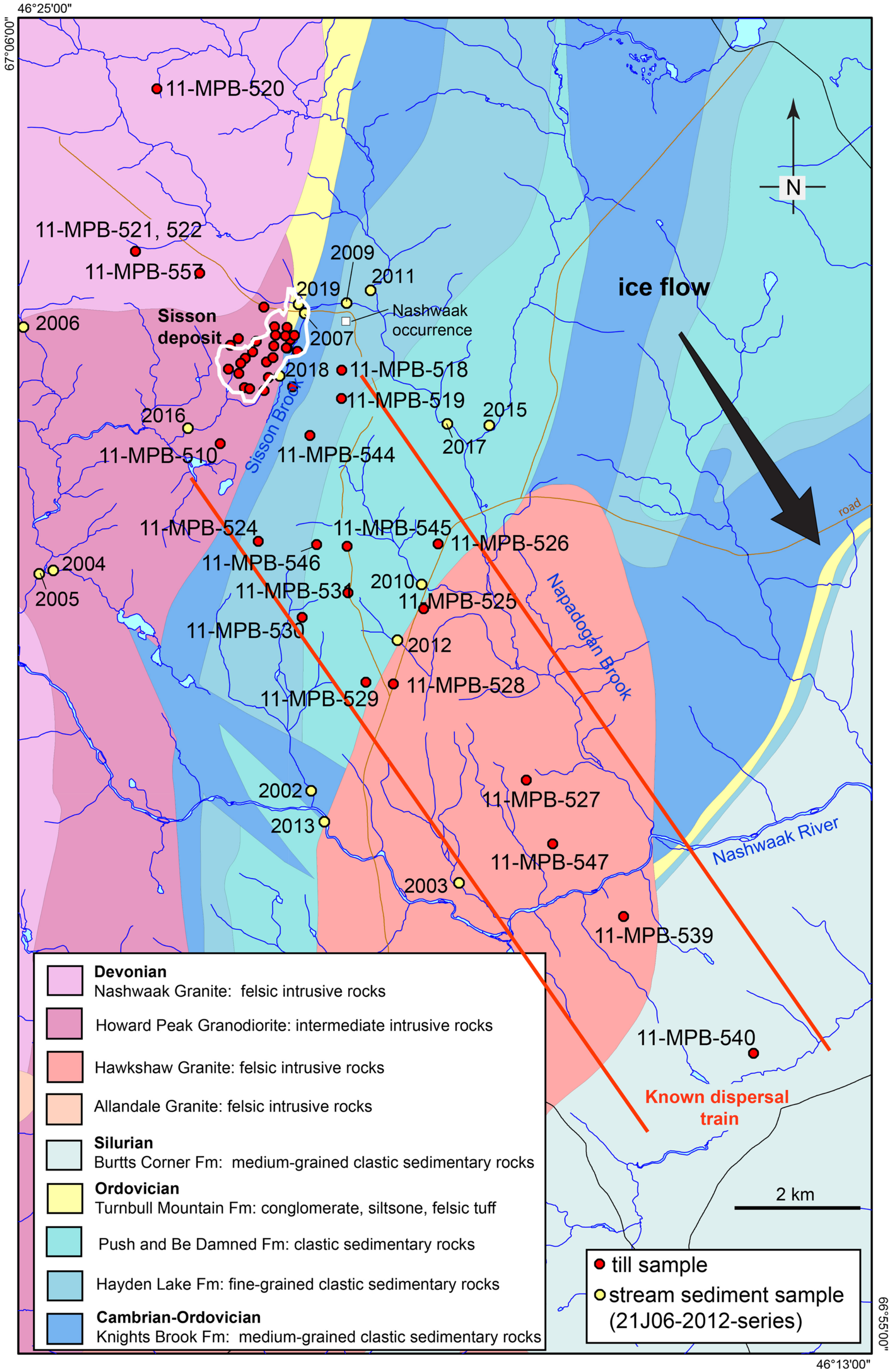

Fig. 2. Local bedrock geology of the Sisson W–Mo deposit area, approximate location of glacial dispersal train (red lines) identified by Seaman & McCoy (2008), and location of till samples (red dots) and stream sediment samples (yellow dots, 21J06-2012- series) up ice (NW), overlying, and down ice (SE) of the deposit. Bedrock geology modified from Smith & Fyffe (2006*b*, *c*, *d*, *e*). White deposit outline from Rennie *et al.* (2013).

Table 1. *Potential indicator minerals of the Sisson W–Mo deposit (from Nast & Williams-Jones 1991; Marr 2009) and those found in bedrock, till and stream sediment samples from this study (McClenaghan et al. 2013a, c, 2014a)*

Mineral	Formula	Specific gravity	Hardness	Size range in bedrock PTS in this study (mm)	Size range in bedrock HMC in this study (mm)	Size range in till HMC in this study (mm)	Size range in stream HMC in this study (mm)	Presence in bedrock reported by others
scheelite	$CaWO_4$	5.9 – 6.1	4 – 5	0.1 – 0.5	0.025 – 2.0	0.025 – 2.0	0.05 – 2.0	Nast & Williams-Jones (1991); Marr (2009)
wolframite	$(Fe,Mn)WO_4$	7.1 – 7.5	4.5	0.04 – 0.08	0.025 – 2.0	0.025 – 1.0	0.015 – 2.0	Nast & Williams-Jones (1991); Marr (2009)
molybdenite	MoS_2	5.5	1.0	≤0.3	0.05 – 2.0	0.075 – 2.0	0.25 – 0.5	Nast & Williams-Jones (1991); Marr (2009)
pyrite	FeS_2	5	6.5	0.015 – 2.2	0.025 – 2.0	0.025 – 0.05	0.05 – 0.5	Nast & Williams-Jones (1991); Marr (2009)
chalcopyrite	$CuFeS_2$	4.1 – 4.3	3.5	0.04 – 2.2	0.1 – 2.0	0.2 – 2.0	0.25 – 0.5	Nast & Williams-Jones (1991); Marr (2009)
sphalerite	(Zn,Fe)S	3.9 – 4.2	3.5 – 4	≤2.2	0.05 – 1.0	0.05 – 2.0	0.25 – 0.5	Nast & Williams-Jones (1991); Marr (2009)
galena	PbS	7.2 – 7.6	2.5	not observed	0.05 – 0.075	0.05	not observed	Nast & Williams-Jones (1991); Marr (2009)
pyrrhotite	$Fe_{(1-x)}S$ (x = 0 – 0.17)	4.6 – 4.7	3.5 – 4	0.05 – 2.2	0.025 – 0.25	not observed	not observed	Nast & Williams-Jones (1991); Marr (2009)
arsenopyrite	FeAsS	6.1	5	not observed	not observed	0.05 – 2.0	0.25 – 0.5	Nast & Williams-Jones (1991); Marr (2009)
bismuthinite	Bi_2S_3	6.8 – 7.2	2.0	not observed	not observed	0.25 – 1.0	not observed	no
bismutite	$Bi_2(CO_3)O_2$	7.0	4.0	not observed	not observed	0.025 – 2.0	not observed	no
native Bi	Bi	9.7 – 9.8	2 – 2.5	0.01	not observed	0.025 – 1.0	not observed	Nast & Williams-Jones (1991); Marr (2009)
joseite	$Bi_4(S,Te)_3$	8.1	2.0	not observed	not observed	0.025 – 0.5	not observed	no

PTS, polished thin section; HMC, heavy mineral concentrate.

(Fig. 2) of the Tetagouche Group. Immediately to the east are quartzite and shale of the Cambro-Ordovician Miramichi Group (Knights Brook Formation). This package of rocks is overlain to the east by additional Tetagouche Group rocks including pyritiferous black shale intercalated with felsic volcanic rocks and mafic volcanic rocks of the Hayden Lake Formation as well as wacke and shale of the Push and Be Damned Formation (Fig. 2). The Tetagouche Group rocks that underlie the east part of the Sisson area are a continuation of the belt of rocks that host the Bathurst Mining Camp volcanogenic massive sulphide (VMS) deposits 100 km to the NW. For this reason, the Tetagouche Group rocks in the Sisson area were the focus of exploration programs from the 1950s into the 1990s. These activities led to the discovery in 1960 of the small but high-grade Nashwaak Pb-Zn-Ag-Sb occurrence (Fig. 2) *c.* 900 m east of the Sisson deposit and, subsequently, the Sisson deposit in 1981. The Nashwaak occurrence is a stratabound pod originally interpreted as a syngenetic VMS showing (e.g. Snow & Coker 1987) and recently interpreted to be a vein-type showing related to the Sisson mineralizing system (Marr 2009; Rennie *et al.* 2013).

Surficial geology

The present-day landscape of the Sisson area is a product of glaciation during the Wisconsinan (110 – 10 ka), during which time glacial sediments were deposited directly on bedrock (Seaman 2004; Stea *et al.* 2011). Bedrock outcrops in the Sisson area are rare due to the locally thick and continuous cover of till that varies from <2 to 20 m. Surface till in the area is a sandy Early Wisconsinan lodgement till likely deposited by SE glacial flow, and possibly reworked by south–SW glacial flow during the Middle to Late Wisconsinan (Escuminac Phase) (Seaman & McCoy 2008). A discontinuous and thin (0.2 – 2.5 m) very loose and very sandy till, deposited by westward flowing ice during the Younger Dryas, overlies the Early Wisconsinan till in a few places (Seaman & McCoy 2008; Fyffe *et al.* 2010; Stea *et al.* 2011). Previous reconnaissance-scale till geochemical surveys in the region identified a 30 km long glacial dispersal train trending SE from the deposit (Figs 2 and 3) that was best defined by varying combinations of W, Mo, As, Bi, Cu, F, Pb and Sn contents in various size fractions of till (Snow & Coker 1987; Lamothe 1992; Seaman 2003, 2012; Seaman & McCoy 2008). Although affected by several ice flows in different directions, only the SE ice flow appears to have dispersed metal-rich debris beyond the deposit.

Regional-scale stream sediment surveys were conducted by the GSC over map areas NTS 21J/07 and 21J/06, which includes the Sisson deposit area. These surveys reported elevated values of W (19 – 86 ppm) and Mo (58 – 437 ppm) in the <0.177 mm (−80 mesh) fraction immediately downstream of the Sisson deposit (Friske *et al.* 2002; Pronk *et al.* 1997).

Field and laboratory methods

Sample locations, site descriptions, photographs and sample depth information are reported in McClenaghan *et al.* (2013*a*, *b*, *c*, 2014*a*, 2015*a*, *b*). Till samples were collected at the Sisson deposit to document the indicator mineral signature at key distances down ice,

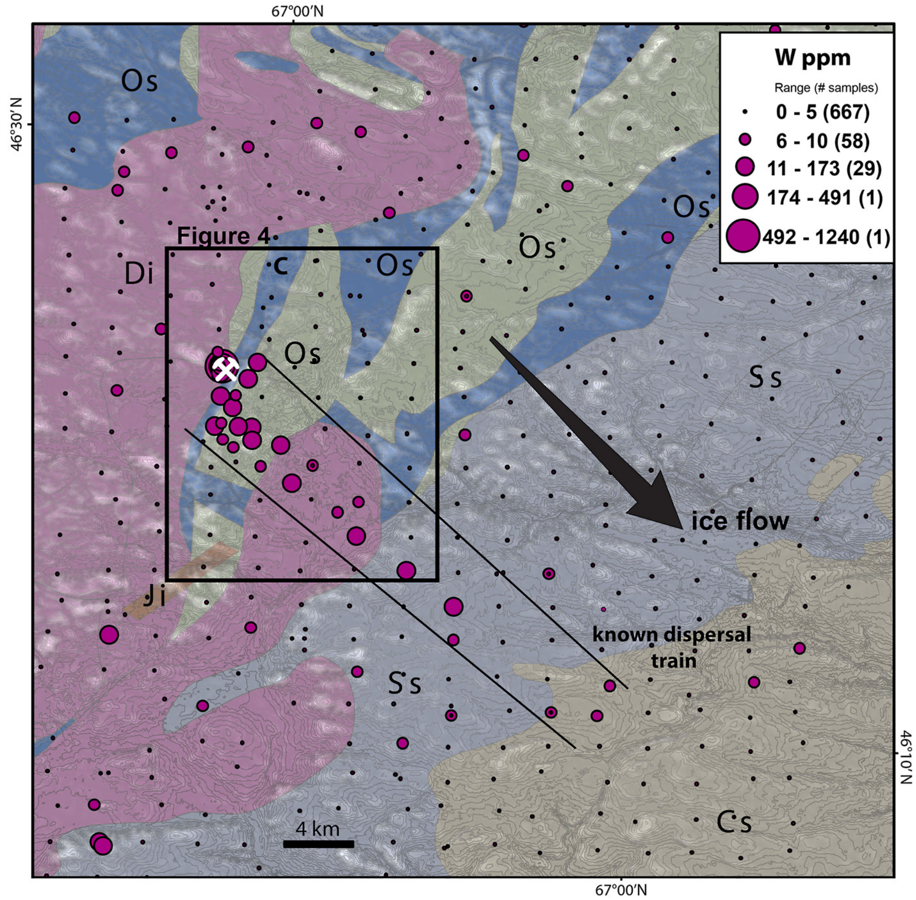

Fig. 3. Proportional dot map of W (INAA) abundance in the <0.063 mm fraction of surface till samples in the Sisson region showing elevated W contents in till 30 km to the SE of the deposit, indicated by the white crossed hammers symbol. Data from Seaman (2003), Seaman & McCoy (2008) and Seaman (2012). Ji, Jurassic intrusive rocks; Di, Devonian intrusive rocks; Ss, Silurian sedimentary rocks; Os, Ordovician sedimentary rocks; C, undivided Cambrian rocks; Cs, Cambrian sedimentary rocks. Bedrock geology modified from Smith & Fyffe (2006*a*–*e*).

and not to remap the known glacial dispersal train. In 2010 and 2011, 60 surface till samples were collected from freshly dug trenches, road cuts and hand-dug holes using GSC sampling protocols described in Spirito *et al.* (2011) and McClenaghan *et al.* (2013*d*). One additional till sample was collected in 2012 over the north end of the deposit. Till samples were mainly collected over the deposit, with additional samples collected 4 km up ice to establish background values in till and up to 14 km down ice of the deposit to sample metal-rich till at varying distances down ice. At each site, three till samples were collected: (1) an 8 – 15 kg sample for recovery of indicator minerals; (2) a 3 kg sample for geochemical analysis of the till matrix and archiving; and, (3) a 200 g sample for in-field testing using a portable XRF to help guide till sampling on a daily basis. Twelve mineralized or host rock samples from the Sisson area were collected from drill core or outcrops to examine the indicator minerals present in polished thin sections (PTS) and heavy mineral concentrates (HMC) (McClenaghan *et al.* 2013*c*).

A total of 16 stream sediment + stream water sites were sampled around the deposit in 2012. These sites were sampled in order to determine heavy mineral abundances at selected distances down stream, and not to conduct a systematic local-scale sampling program. Samples were collected using GSC National Geochemical Reconnaissance (NGR) sampling protocols similar to those reported by Day *et al.* (2013) and McCurdy & McNeil (2014). At each site, three samples were collected: (1) a 9 – 14 kg stream sediment sample for the recovery of indicator minerals; (2) an *c.* 200 g fine grained sediment sample for geochemical analysis and archiving; and (3) a 60 ml filtered (0.45 µm) stream water sample for geochemical analysis.

The <0.063 mm (−250 mesh) fraction of till was analyzed using modified aqua regia/ICP-MS on a 0.5 g aliquot. A separate 0.2 g aliquot was analysed by lithium metaborate/tetraborate total fusion decomposition followed by nitric acid digestion/ICP-ES, ICP-MS at ACME Laboratories, Vancouver (now Bureau Veritas Minerals Labs). 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 historic till samples, previously analyzed by NBDERD as part of their regional surveys, were re-analyzed at the same time. The <0.177 mm (−80 mesh) fraction of stream sediment was analyzed for total trace elements using INAA on a 30 g aliquot at Becquerel Laboratory, Mississauga (now Maxxam Analytics) and modified aqua regia/ICP-MS on a 0.5 g aliquot at ACME Laboratories. Filtered water samples were acidified and analyzed at GSC-Ottawa for trace elements by ICP-MS and major elements by ICP-ES. Detailed descriptions of till, stream sediment and stream water analytical methods, monitoring of analytical accuracy and precision and data listings are reported in McClenaghan *et al.* (2013*b*, 2014*b*, 2015*a*).

Bedrock, till and stream sediment heavy mineral samples were processed at the commercial laboratory Overburden Drilling Management Limited (ODM), Ottawa, to recover a heavy mineral concentrate (HMC) and determine the abundance of indicator minerals in each sample. Prior to processing, bedrock samples were disaggregated using a CNT-MC Inc. Spark 2 electric pulse disaggregator to preserve natural grain sizes, textures and shapes (Lastra *et al.* 2003; Cabri *et al.* 2008; McClenaghan 2011). The <2.0 mm fraction of each bedrock, till and stream sediment sample was processed at ODM to produce a non-ferromagnetic HMC using a combination of tabling and heavy liquids (specific gravity (SG) 3.2) using procedures outlined in McClenaghan *et al.* (2013*a*, *c*, 2014*a*, 2015*a*). The 0.25 – 0.5, 0.5 – 1.0, and 1.0 – 2.0 mm non-ferromagnetic HMCs of each sample were then examined. Potential indicator minerals of W–Mo mineralization were counted and some grains removed for detailed study. To allow comparisons of results between till and stream sediments samples, indicator mineral abundances reported in the text, tables and figures are normalized to

Fig. 4. Colour photographs of indicator mineral grains from till samples from around the Sisson W–Mo deposit: (**a**) scheelite under visible light from till sample 11-MPB-507; (**b**) scheelite under short-wave ultraviolet light from till sample 11-MPB-507; (**c**) black wolframite from till sample 12-MPB-1026; (**d**) molybdenite from till sample 11-MPB-567; (**e**) spessartine from till sample 11-MPB-518. Photographs taken by Michael Bainbridge Photography. Please see online version for colour.

a 10 kg mass of the <2 mm fraction. All counts reported in the text are for the 0.25 – 0.5 mm HMC fraction unless otherwise stated. As part of this study, a systematic method was developed to examine individual HMCs inside a black box using short-wave ultraviolet light to rapidly and consistently determine the scheelite content. Under visible light, scheelite has an unremarkable pale yellow colour (Fig. 4a), but under short-wave ultraviolet light it has a diagnostic bright bluish white fluorescence (Fig. 4b) that changes to yellow with increasing Mo content.

Results

Indicator minerals in bedrock, till and stream sediments

Indicator mineral data for bedrock, till and stream sediment samples up ice, overlying, and down ice/down stream of the Sisson deposit, including QA-QC data, are reported in McClenaghan *et al.* (2013*a*, *c*, 2014*a*, 2015*a*) and summarized in Tables 2 and 3. Table 2 reports data for selected till samples within or proximal to the glacial

Table 2. *Abundance of selected indicator minerals in the non-ferromagnetic heavy mineral fraction of selected till samples, normalized to 10 kg of <2 mm table feed, compared to the content of total W (borate fusion/ICP-MS), Mo, As, Bi and Cu (aqua regia/ICP-MS) in the <0.063 mm fraction of till. Samples are listed according to increasing distance down ice (SE) of the Sisson W–Mo deposit (modified from McClenaghan et al. 2013*b*, 2014*b*)*

Till sample	Location	Distance from deposit (m)	Scheelite 0.25 – 0.5 mm	Scheelite 0.5 – 2.0 mm	Wolfram 0.25 – 0.5 mm	Wolfram 0.5 – 2.0 mm	Moly 0.25 – 0.5 mm	Moly 0.5 – 2.0 mm	Chalco 0.25 – 0.5 mm	Chalco 0.5 – 2.0 mm	Arseno 0.25 – 0.5 mm	Sphalerite 0.25 – 0.5 mm	Bi minerals 0.25 – 0.5 mm	Pyrite 0.25 – 0.5 mm	Spess 0.25 – 0.5 mm	W ppm	Mo ppm	Bi ppm	As ppm	Cu ppm
11-MPB-520	background up ice	−4000	0	0	0	0	0	0	0	0	0	0	0	0	1	6	0.5	1.2	11	16
11-MPB-521	background up ice	−2250	2	0	0	0	0	0	0	0	0	0	0	0	0	4	0.6	1.0	14	23
	threshold		***2***	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***1***	***7***	***1.7***	***1.8***	***92***	***87***
11-MPB-507	overlying mineralization	0	4706	150	0	0	0	0	0	0	0	0	0	0	0	816	63.0	13.5	114	310
11-MPB-513	overlying mineralization	0	83	12	0	0	0	0	2	1	0	14	1	0	0	113	1.7	33.3	80	456
11-MPB-567	overlying mineralization	0	261	44	0	0	87	49	8	2	0	0	2	217	2	92	58.6	10.2	58	107
11-MPB-568	overlying mineralization	0	450	94	0	0	4	2	7	2	1	1	1	18	0	325	58.3	14.4	106	320
11-MPB-573	overlying mineralization	0	1852	78	0	0	4	0	0	0	0	0	4	2	0	393	36.4	6.7	28	184
12-MPB-1026	overlying mineralization	0	280	17	112	36	0	0	2	0	1	0	0	1	1	54	4.2	14.8	537	271
11-MPB-574	proximal down ice	20	5	4	0	0	0	0	1	0	7	0	0	29	0	42	4.5	6.7	39	104
11-MPB-502	proximal down ice	50	40	2	0	0	0	0	6	0	0	0	2	1200	4	48	1.6	41.7	257	400
11-MPB-562	proximal down ice	100	404	44	0	0	0	0	1	0	0	0	1	10	0	14	1.1	8.3	21	84
11-MPB-511	proximal down ice	400	36	0	0	0	0	0	2	0	0	0	0	0	183	65	3.7	7.9	37	134
11-MPB-519	proximal down ice	1100	6	1	0	0	0	0	0	0	0	0	0	0	1042	41	8.0	12.7	174	125
11-MPB-544	proximal down ice	1100	49	8	0	0	0	0	1	0	0	0	0	0	5	75	8.3	6.1	79	179
11-MPB-546	distal down ice	2500	2	0	0	0	0	0	2	1	0	0	1	0	17	16	1.0	7.6	71	84
11-MPB-526	distal down ice	3600	2	0	0	0	0	0	0	0	0	0	0	0	440	13	1.6	2.8	62	95
11-MPB-531	distal down ice	4000	3	0	0	0	0	0	0	0	0	0	4	0	0	14	1.6	6.7	81	93
11-MPB-525	distal down ice	4300	8	0	0	0	0	0	0	0	0	0	0	0	17	22	1.6	3.5	47	59
11-MPB-539	distal down ice	10 000	7	0	0	0	0	0	0	0	0	0	0	0	0	13	0.9	1.6	22	31
11-MPB-540	background down ice	13 000	0	0	0	0	0	0	0	0	0	0	0	0	17	4	6.0	0.6	24	35

Wolfram, wolframite; Moly, molybdenite; Chalco, chalcopyrite; Arseno, arsenopyrite; Spess, spessartine.

Table 3. *Abundance of selected indicator minerals in the 0.25 – 0.5 mm non-ferromagnetic heavy mineral fraction of stream sediment samples, normalized to 10 kg of <2 mm table feed, compared to the content of total W, Mo (INAA), As and Bi (aqua regia/ICP-MS) in the <0.177 mm fraction of stream sediment and in stream water. Samples are listed according to increasing distance downstream of the Sisson W–Mo deposit (modified from McClenaghan et al. 2015a)*

Stream sediment sample	Location	Distance down stream from deposit (m)	Scheelite 0.25 – 0.5 mm	Scheelite 0.5 – 2.0 mm	Wolfram 0.25 – 0.5 mm	Wolfram 0.5 – 2.0 mm	Moly 0.25 – 0.5 mm	Chalco-pyrite 0.25 – 0.5 mm	Arseno-pyrite 0.25 – 0.5 mm	Sphalerite 0.25 – 0.5 mm	Pyrite 0.25 – 0.5 mm	Spess 0.25 – 0.5 mm	W ppm stream silt	W ppb stream water	Mo ppm stream silt	Mo ppb stream water	As ppm stream silt	As ppb stream water	Bi ppm stream silt
21J06-2012-2004	background upstream	−7.0	3	0	0	0	0	0	0	0	0	0	7	<0.02	1	0.11	5	0.9	0.1
21J06-2012-2006	background upstream	−6.0	8	1	0	0	0	0	0	0	0	0	5	<0.02	<1	0.10	34	2.6	0.2
21J06-2012-2015	background upstream	−4.0	5	3	0	0	0	0	0	0	1	0	2	<0.02	1	0.12	16	0.8	0.2
21J06-2012-2011	background upstream	−1.5	2	0	0	0	0	1	1	1	2475	2970	3	<0.02	1	0.14	34	1.2	0.5
	threshold		***8***	***3***	***0***	***0***	***0***	***1***	***1***	***1***	***2475***	***2970***	***7***	***<0.02***	***1***	***0.14***	***34***	***2.6***	***0.5***
21J06-2012-2007	overlying	0.0	2041	291	153	105	2	2	2	0	0	0	197	0.64	69	6.60	169	2.2	4.7
21J06-2012-2018	overlying	0.0	128	44	1	0	0	0	0	0	0	26	23	0.47	3	0.63	3	1.5	0.3
21J06-2012-2019	overlying	0.0	300	60	5	0	0	0	0	0	0	0	42	0.11	19	0.38	55	0.9	4.6
21J06-2012-2009	downstream	0.5	730	36	36	4	0	0	0	0	0	0	115	0.53	18	3.66	79	4.2	3.7
21J06-2012-2016	downstream	1.0	0	0	0	0	0	0	0	0	4	0	18	0.57	39	7.54	13	3.3	0.5
21J06-2012-2017	downstream	4.0	75	17	12	6	0	4	0	0	7	14 151	6	0.06	5	0.51	45	1.4	1.0
21J06-2012-2005	downstream	4.5	2	3	0	0	0	0	0	0	1	4	2	0.04	3	0.44	12	1.1	0.3
21J06-2012-2012	downstream of dispersal train	5.0	75	7	0	0	0	3	0	0	1	9	33	0.02	2	0.14	29	1.0	2.6
21J06-2012-2002	downstream of dispersal train	6.5	0	0	0	0	0	0	0	0	1	0	2	<0.02	2	0.12	44	1.3	0.2
21J06-2012-2003	downstream of dispersal train	9.5	0	0	0	0	0	0	0	0	0	190	8	0.02	1	0.34	6	0.9	0.3
21J06-2012-2013	downstream	16.0	7	1	0	0	0	2	0	0	19	19	3	<0.02	2	0.24	15	0.8	0.3

Wolfram, wolframite; Moly, molybdenite; Chalco, chalcopyrite; Arseno, arsenopyrite; Spess, spessartine.

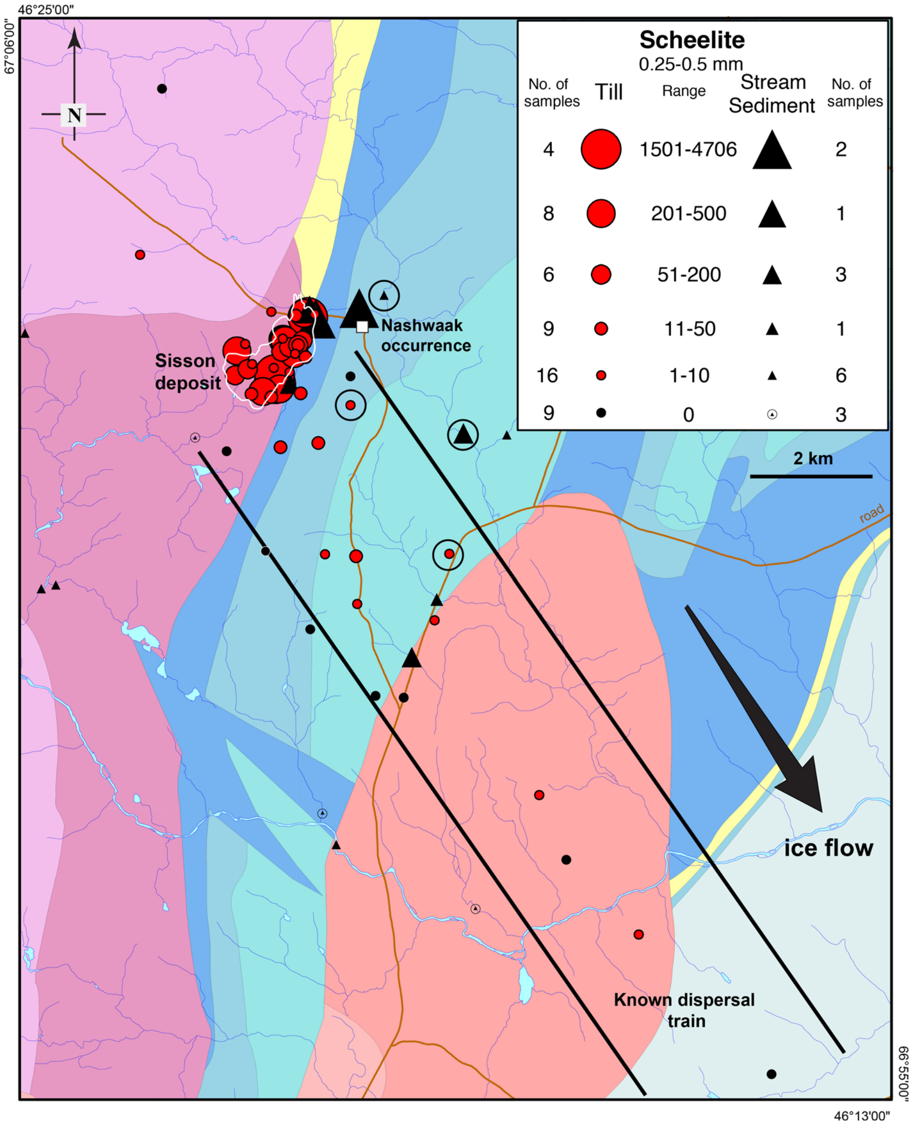

Fig. 5. Proportional symbol map of scheelite abundance in the 0.25 – 0.5 mm non-ferromagnetic fraction heavy mineral (specific gravity >3.2) of surface till samples (red dots) and stream sediments (black triangles) around the Sisson W–Mo deposit. Bedrock geology modified from Smith & Fyffe (2006*b*, *c*, *d*, *e*). Deposit outline in white is from Rennie *et al.* (2013) Bedrock geology legend same as in Figure 2. Grain counts normalized to 10 kg table feed (<2 mm). Large black circles around four sites indicate samples with significant spessartine contents discussed in text.

dispersal train that was defined by Seaman (2003) and Seaman & McCoy (2008), listed by location relative to the Sisson deposit: up ice, proximal up ice (within 200 m of the deposit), overlying, proximal down ice (within 1000 m of the deposit), and distal down ice (>1000 m down ice). Table 3 lists data for stream sediment samples organized by location relative to the deposit and the known glacial dispersal train.

Ore indicator minerals in bedrock samples include scheelite, wolframite and molybdenite (Fig. 4) and all three minerals were recovered from till and stream sediment samples. Scheelite is by far the most abundant ore indicator mineral in till (maximum 4706 grains) and stream sediment (maximum 2137 grains) (Fig. 5). Background scheelite contents of till range from 0 to 2 grains and in stream sediment from 0 to 8 grains. Wolframite is far less abundant than scheelite in both till (maximum 112 grains) and stream sediment (maximum 214 grains) and was only recovered from one till sample and 5 stream sediment samples. Background wolframite content in both till and stream sediment is zero grains. Molybdenite is also rare in both till (maximum 87 grains) and stream sediment (maximum 2 grains) and only recovered from 11 till samples and one stream sediment sample. Background content of molybdenite in both till and stream sediment is zero grains. Additional indicator minerals recovered from till overlying and down ice of the deposit include Bi minerals (joseite, native Bi, bismutite, bismuthinite) (Fig. 6a–c), galena, sphalerite, pyrite (Fig. 6d), chalcopyrite (Fig. 6e) and arsenopyrite (Fig. 6f). Some till and stream sediment samples overlying and immediately down ice, or downstream, contain ones to tens of grains of these minerals (Tables 2 and 3).

Most till and stream sediment samples contain between 0 and 50 spessartine grains. However, two till samples (11-MPB-519, 11-MPB-526) are noteworthy because they contain >400 grains each (Tables 2 and 3). Stream sediment samples 21J06-2012-2011 and 21J06-2012-2017 each contain >1000 grains (Table 3). These four samples overlie Tetagouche Group Ordovician rocks to the NE and east of the deposit (Fig. 2).

Scheelite grains up to 2 mm in size were recovered from each of bedrock, till and stream sediment samples, although scheelite is most abundant in the 0.25 – 0.5 mm fractions of each media type. Coarse scheelite (0.5 – 2.0 mm) was recovered from till up to 2.5 km down ice and from stream sediment up to 5 km downstream of the deposit + glacial dispersal train. Similar to scheelite, the minerals wolframite, molybdenite, chalcopyrite, sphalerite and bismutite are most abundant in the finer till fractions (0.25 – 0.5 mm), but also exist as coarse (1.0 – 2.0 mm) grains proximal to the deposit.

Till geochemistry

Till geochemical data, including QA-QC data, are reported in McClenaghan *et al.* (2013*b*, 2014*b*). Data for standards, duplicates and blanks indicate that the analytical data reported are acceptable. Results for till samples are summarized in Table 2 and are listed by

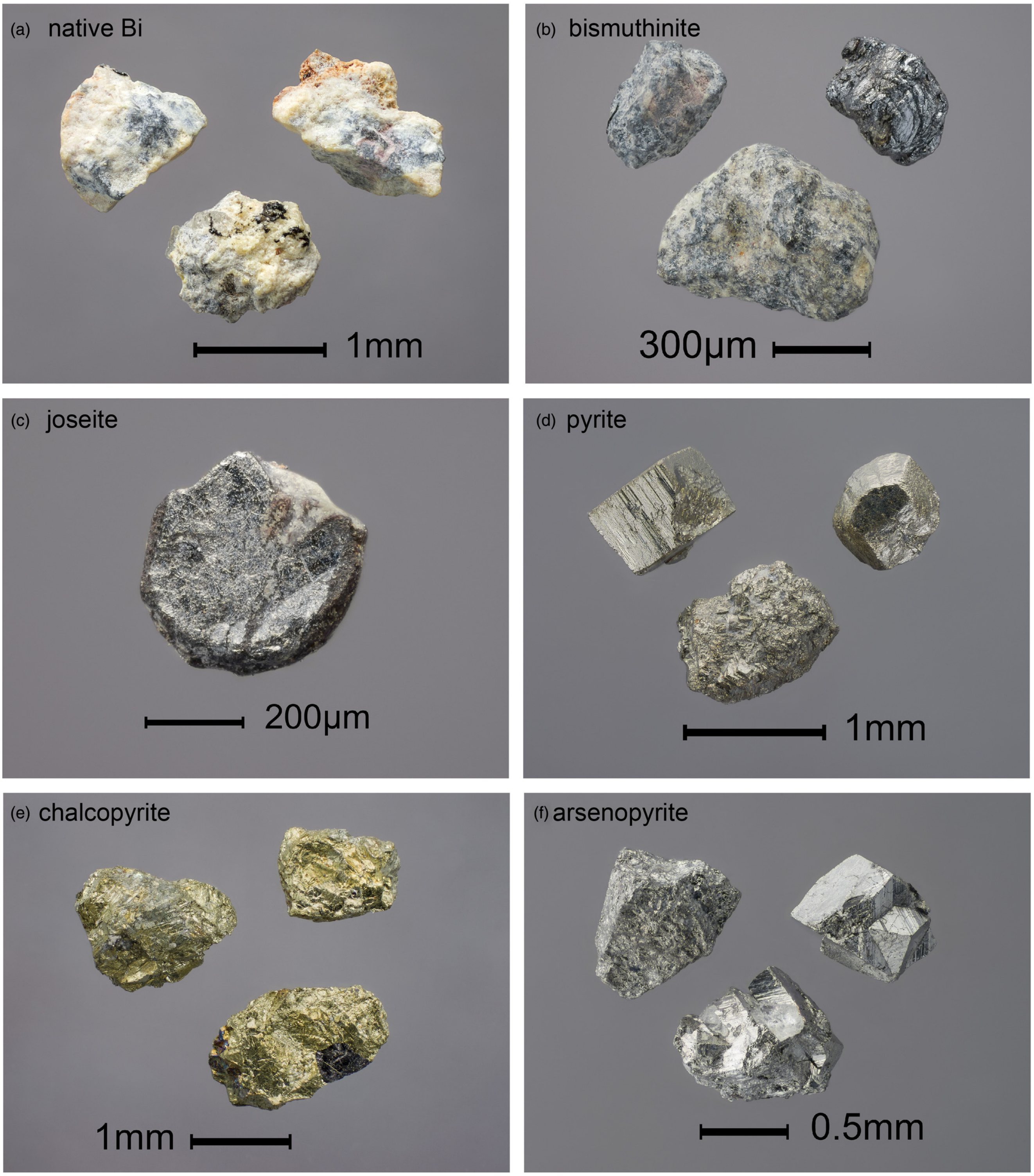

Fig. 6. Colour photographs of indicator mineral grains from till samples from around the Sisson W–Mo deposit: (**a**) native Bi (silver mineral) from till sample 11-MPB-513; (**b**) bismuthinite from till sample 11-MPB-567; (**c**) joseite from till sample 11-MPB-573; (**d**) pyrite from till sample 11-MPB-535; (**e**) chalcopyrite from bedrock sample 11-MPB-R05; (**f**) arsenopyrite from till sample 11-MPB-534. Photographs taken by Michael Bainbridge Photography. Please see online version for colour.

location relative to the Sisson deposit. The table also reports threshold values between and anomalous background till samples that were established using data for 9 'background' till samples (3 GSC, 6 historic NBDERD samples) located between 1 and 4 km up ice (north and NW) of the deposit (see Table 2 in McClenaghan *et al.* 2013*b*).

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 and the term 'pathfinder element' is used here to refer to non-ore elements associated with the orebody that may be used to detect the orebody (Rose *et al.* 1979). Indicator elements in till for the Sisson deposit include total W (Fig. 7) and Mo (Table 4). Pathfinder elements include Pb (Fig. 8), Ag, As, Bi, Cd, Cu, In, Te and Zn (Table 4). This extensive suite of elements is more than the few elements (W, Mo, Cu, As and F) identified by Snow & Coker (1987),

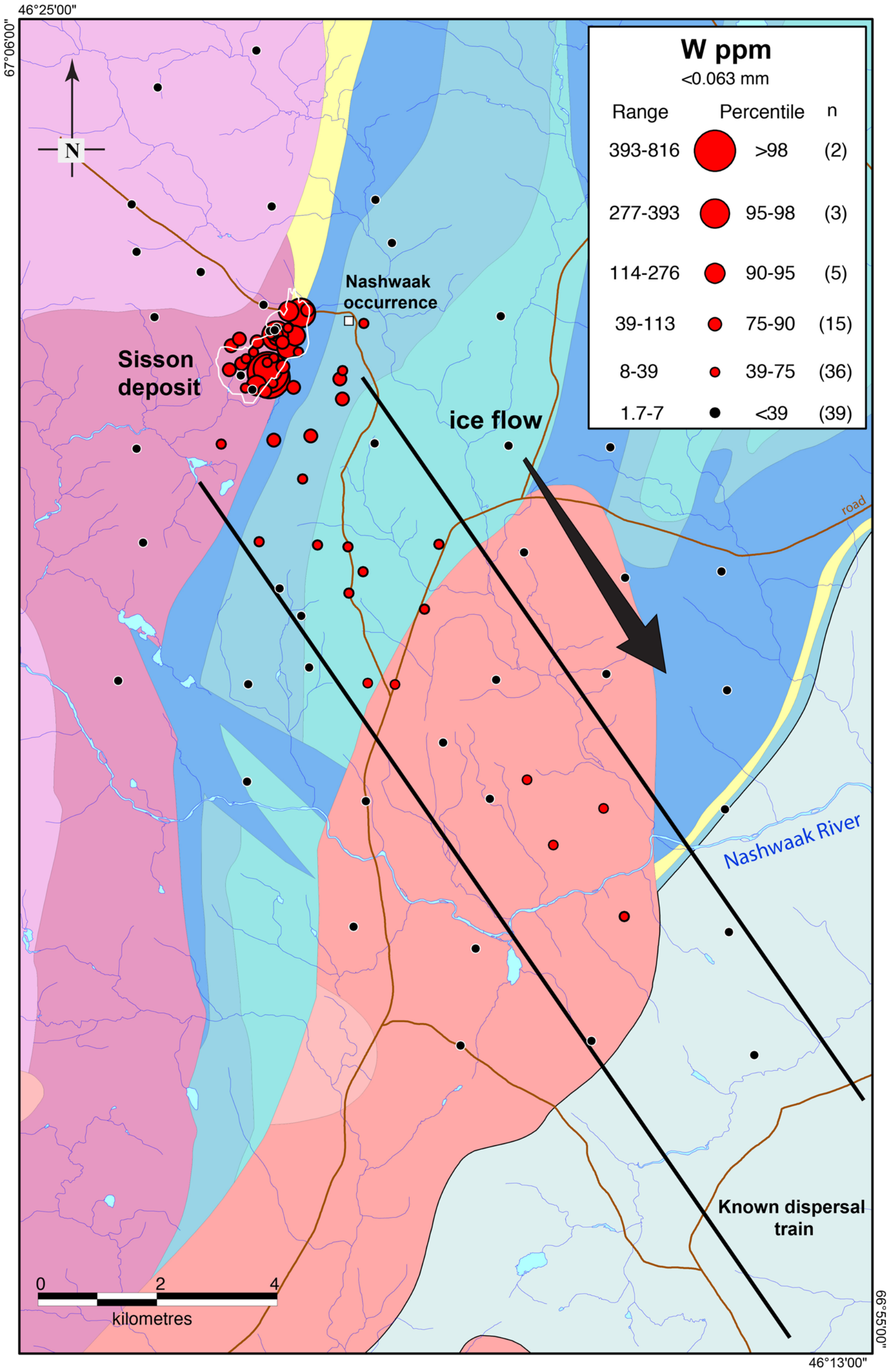

Fig. 7. Proportional dot map of W (borate fusion/ICP-MS) abundance in the <0.063 mm fraction of surface till samples around and down ice of the Sisson deposit. Bedrock geology modified from Smith & Fyffe (2006*b*, *c*, *d*, *e*). Deposit outline in white from Rennie *et al.* (2013). Bedrock geology legend same as in Figure 2.

Lamothe (1992), and Seaman & McCoy (2008) in their earlier till geochemical studies around the deposit.

Elevated concentrations of 474 ppm Pb (Fig. 8), Ag, As, Cu, In Te and Zn are also present in till east and NE of the Sisson deposit. The bedrock source(s) of these metals is presently unknown. These elevated concentrations may reflect: (1) SE glacial dispersal from a more distal expression of the intrusion that formed the Sisson deposit; or (2) glacial dispersal from unrelated metal-rich Ordovician Tetagouche Group sedimentary rocks to the north and east.

Stream sediment and water geochemistry

Geochemical data for stream sediments and water, along with QA-QC data, are reported in McClenaghan *et al.* (2015*a*). Data for standards, duplicates and blanks indicate that the analytical data reported are acceptable and free of contamination. Results for samples are summarized in Table 3 organized by location relative to the Sisson deposit. The table also reports threshold and anomalous background values for stream sediment and water samples established assuming that the four samples between 1.5 and 7 km upstream represent background. Total W values in stream silt vary from background values of 2 – 7 ppm, to a high of 297 ppm overlying the deposit (Fig. 9). The highest values are higher than the highest value (86 ppm) that was reported for regional stream silt samples in the local area (Pronk *et al.* 1997; Friske *et al.* 2002).

Molybdenum contents in stream silt varies from background values of <1 – 1 ppm, to a high of 69 ppm. This range of values is considerably lower than the values (58 – 437 ppm) reported by Friske *et al.* (2002) and Pronk *et al.* (1997). Indicator/pathfinder elements in the <0.177 mmm fraction of stream sediment down stream of the Sisson deposit include W (INAA) and Mo, as well as Ag, As, Bi, Cd, Cu, In, Tl and Zn (Table 4). This suite of elements is

Table 4. *Summary of indicator minerals and indicator and pathfinder elements in till, stream sediment and stream waters around the Sisson W–Mo deposit (modified from McClenaghan et al. 2015b)*

Media	Indicator/pathfinder elements	Indicator minerals
bedrock	*not determined*	scheelite, wolframite, molybdenite, chalcopyrite, sphalerite, galena, pyrite, native Bi, pyrrhotite
till	Ag, As, Bi, Cd, Cu, In, Mo, Pb, Te, W, Zn,	scheelite, wolframite, molybdenite, chalcopyrite, Bi-rich minerals (joseite, native Bi, bismutite, bismuthinite), galena, sphalerite, arsenopyrite, pyrite
stream sediment	Ag, As, Bi, Cd,Cu, In, Mo, Tl, W, Zn	scheelite, wolframite, molybdenite, chalcopyrite, sphalerite, arsenopyrite, pyrite
stream water	As, Cd, Cu, Cs, Mo, W, Zn	

more extensive than those (W, Cd, Pb, Ag, Zn) identified in previously reported regional stream sediment surveys (Pronk *et al.* 1997; Friske *et al.* 2002) that included the Sisson area. Elevated concentrations of indicator/pathfinder elements in stream waters around the Sisson deposit include W (Fig. 10), As, Cd, Cu, Cs, Mo and Zn (Table 4). Tungsten values in stream water vary from <0.02 ppb in background samples to a high of 0.64 ppb overlying the deposit.

Discussion

Indicator minerals of W–Mo mineralization

The primary Sisson ore minerals recovered from bedrock, till and stream sediment samples in this study are scheelite, wolframite and molybdenite. They are heavy minerals (Table 1) that are visually distinct and easily recovered by routine sample processing methods such as tabling and heavy liquid separation (McClenaghan 2011) used in this study. Other indicator minerals in till and stream sediment samples overlying and down ice of the Sisson deposit include chalcopyrite, joseite, native Bi, bismutite, bismuthinite, galena, sphalerite, arsenopyrite, pyrrhotite, pyrite (Table 4) and these reflect the polymetallic nature of the deposit.

Most earlier reports describing the use of indicator minerals in till for W–Mo exploration were published between the 1970s and early 1990s and focused on the recovery of scheelite (e.g., Brundin & Bergström 1977; Toverud 1984; Johansson *et al.* 1986). These older studies used heavy mineral recovery methods that were unique to each study and not available from a commercial laboratory. The mineralogical examinations were commonly carried out on a sample only after it was identified geochemically to be W-rich. Recovery of W–Mo indicator minerals is now available in commercial heavy mineral processing laboratory using modern methods (shaking table, heavy liquid separation, centrifugal separator, spiral separator) that are consistent between samples and batches, timely and cost effective (McClenaghan 2011). The extensive list of indicator minerals identified for the Sisson deposit reflects the ability of indicator mineral methods to recover and recognize a broad range of minerals. Colour photographs of the key minerals are provided here (in the online version) for the first time to demonstrate their physical characteristics that allow them to be identified (e.g. colour, cleavage, fluorescence).

The advantages of indicator mineral methods over traditional geochemical analysis of <0.063 mm or heavy mineral fractions are that the indicator mineral grains: (1) are visible and can be examined with a binocular or scanning electron microscope; (2) can be analyzed to provide information about the nature of the mineralizing system (e.g., Poulin *et al.* in press); (3) provide physical evidence of the presence or absence of mineralization or alteration; (4) provide information about the source that traditional geochemical methods cannot, including nature of the ore, alteration, and proximity to source; and (5) are the equivalent of ppb detection levels where there are just a few grains in a 10 kg samples (Brundin & Bergström 1977; Averill 2001).

The bedrock source of large spessartine abundances in till samples that overlie Ordovician sedimentary rocks of the Tetagouche Group is not known. Gardiner & Venugopal (1992) reported the presence of spessartine in the Sisson deposit, thus the grains in the till and stream sediments may be derived from the Sisson mineralizing system. The possibility also exists that the grains may have been eroded from alteration zones associated with metamorphosed massive sulphide mineralization (Averill 2001) in Tetagouche Group rocks NE of the deposit, or from other regional metamorphosed rocks. Elevated concentrations of Pb, Ag, As, Cu, In Te and Zn in till also overlie Tetagouche Group sedimentary rocks. The elevated spessartine and trace elements contents may reflect: (1) dispersal from a more distal expression of the intrusion that formed the Sisson deposit; or (2) dispersal from unrelated metal-rich Tetagouche Group sedimentary rocks to the north and east.

Distance of transport

The indicator mineral abundances for surface till samples reported in Table 2 provide abundance v. distance of glacial transport from a W–Mo mineralized source. Of all the indicator minerals identified in this study, scheelite has been glacially dispersed the greatest distance down ice (at least 10 km). Wolframite is rare in the deposit. It was recovered only from one till sample that directly overlies the wolframite-bearing zone in the NE corner of the deposit. Molybdenite was recovered only from till directly overlying the deposit, indicating the extreme softness of molybdenite (hardness = 1) and its inability to survive glacial transport. Bismuth-bearing minerals were recovered from till at least 4 km down ice (SE). Sulphide minerals are present in till overlying the deposit (sphalerite, galena, arsenopyrite, chalcopyrite, pyrite) and up to 5 km down ice (chalcopyrite, pyrite).

The Sisson deposit is covered by 3 to >8 m of till; no streams directly erode the bedrock surface of the deposit. Thus, indicator minerals recovered in stream sediments are presumed to have been eroded from the till (Fig. 11). Indicator mineral abundances in stream sediment samples are summarized in Table 3 along with their estimated distance downstream from the deposit or from the glacial dispersal train. Data in the table may be used as a guide as the minerals that might be expected at varying distances of glacial + fluvial transport distance away from a W–Mo mineralized source in glaciated terrain. Scheelite was recovered from stream sediment at least 4 km directly downstream from the deposit as well as in streams 4 km to the SE, that directly drain the glacial dispersal train. Wolframite was recovered from stream sediment samples that directly overlie the NE corner of the deposit and at least 4 km downstream from this part of the deposit. The greater abundance of wolframite in streams v. till may reflect the concentration of this dense (SG = 7.1 – 7.5) mineral during fluvial transport and the proximity of the stream to the wolframite-bearing till overlying the north end of the deposit. Molybdenite was recovered only from stream sediment directly overlying the deposit which likely reflects the mineral's extreme softness and inability to survive glacial and fluvial transport. No Bi-bearing minerals were recovered from stream sediment samples. Sulphide minerals are present in stream sediment overlying the deposit (sphalerite, arsenopyrite, chalcopyrite, pyrite) in some samples downstream.

The glacial dispersal of indicator minerals and metal-rich fine fraction of till resulted in a dispersal signature that is estimated to be

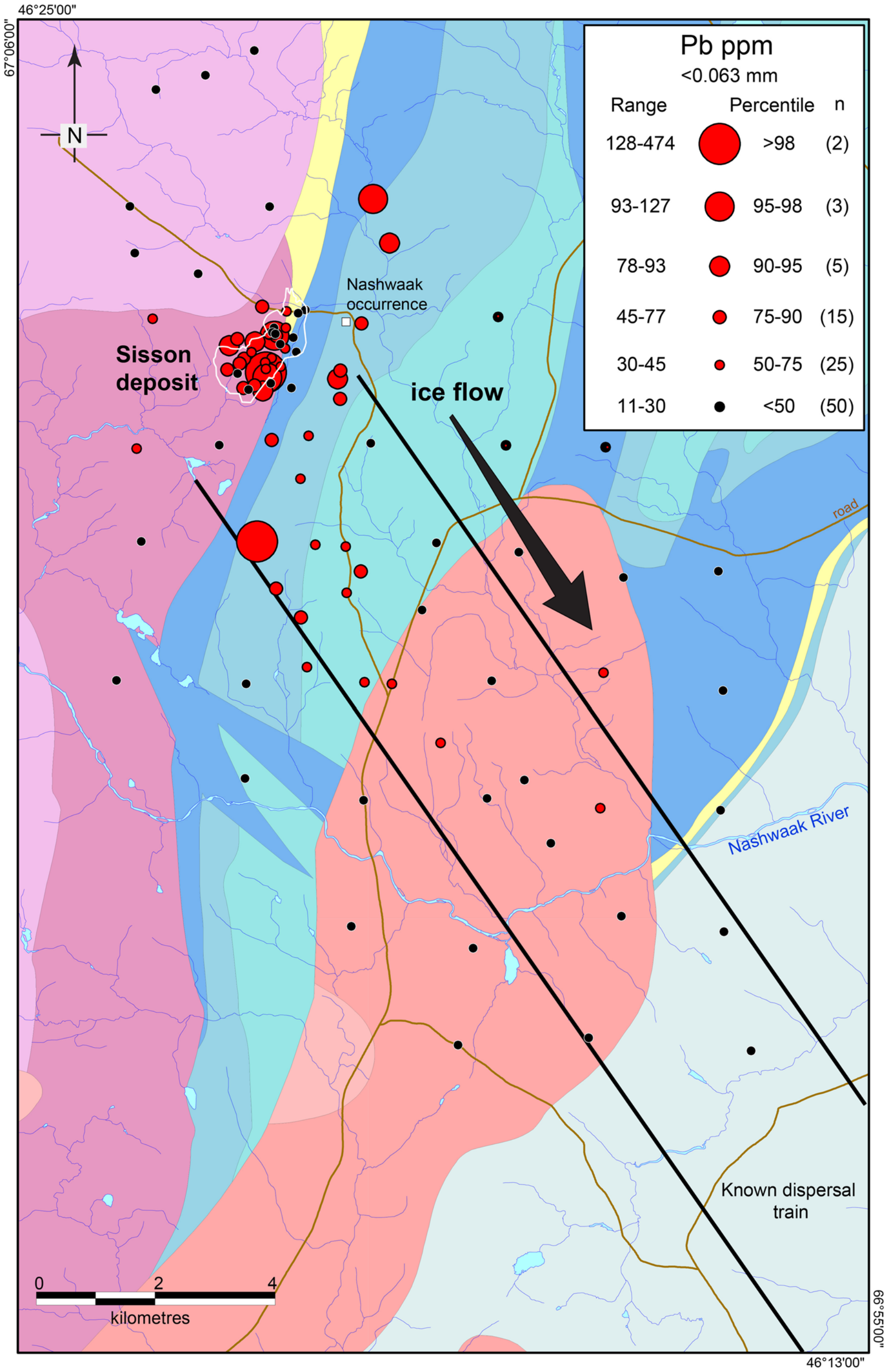

Fig. 8. Proportional dot map of Pb (aqua regia/ICP-MS) abundance in the <0.063 mm fraction of surface till samples around and down ice of the Sisson deposit. Bedrock geology modified from Smith & Fyffe (2006*b*, *c*, *d*, *e*). Deposit outline in white from Rennie *et al.* (2013). Bedrock geology legend same as in Figure 2.

at least 14 km long ×2 km wide (28 km^2). The geochemical and indicator mineral signature of the stream sediments is estimated to be *c.* 8 km^2. The stream water signature of the deposit is estimated to be *c.* 16 km^2. All three media form much larger exploration targets than the actual deposit (1.6 km^2) and thus are well suited to intrusion-hosted W–Mo exploration in glaciated terrain. In this study, both till and stream sediment sampling are of comparable cost and effectiveness in the identification of transported heavy mineral and geochemical anomalies.

Sources of high metal contents in till, stream sediment and water

The Sisson deposit contains an estimated resource of 383 Mt at 0.069% WO_3 (Rennie *et al.* 2013) thus it is not unexpected for a deposit that subcrops under glacial sediments for the fine fraction of till or stream sediment to contain significant (hundreds ppm) W concentrations, the HMC fraction to contain hundreds to thousands of scheelite grains (Tables 2 and 3), and for stream water to contain elevated W (tens to hundreds ppt). Rennie *et al.* (2013) also reported that the Sisson deposit has a significant grade of Mo (0.023%) hosted by molybdenite and Mo-rich scheelite. As a result, till and stream silts overlying and downstream of the deposit contain tens of ppm Mo and stream waters contain hundreds to thousands of ppt Mo. Only a few till samples and one stream sediment HMC sample contain molybdenite grains because it is too soft to survive glacial and/or fluvial transport.

Elevated Cu values (hundreds ppm) in some till, stream sediment and stream water samples at Sisson likely reflect the presence of chalcopyrite in the mineralized rocks. Sphalerite is likely the source of elevated Zn in till and stream sediments as well as a source for trace elements (Cd, In, Tl) that Cook *et al.* (2009) and Pfaff *et al.* (2011) have reported can be present in sphalerite. Silver bearing minerals in the deposit include hessite and acanthite (Nast &

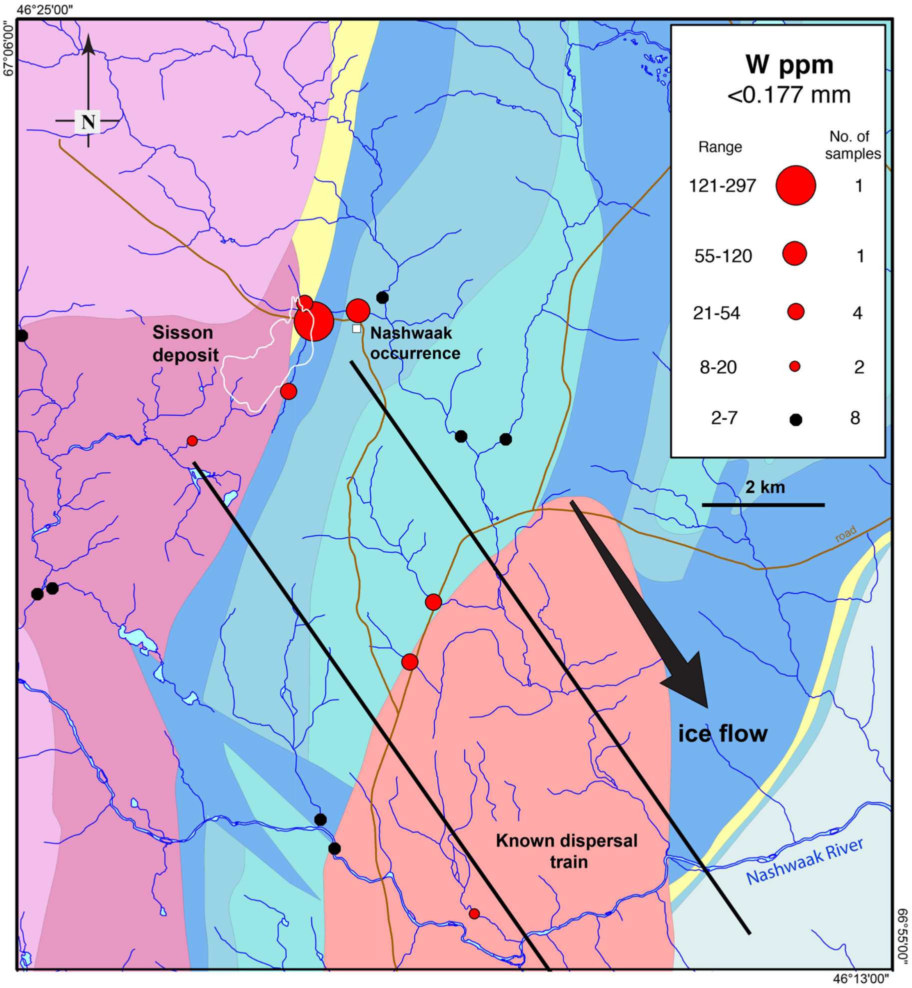

Fig. 9. Proportional dot map of W (INAA) abundance in the <0.177 mm fraction of stream sediment samples around and downstream of the Sisson deposit. Bedrock geology modified from Smith & Fyffe (2006*b*, *c*, *d*, *e*). Deposit outline in white from Rennie *et al.* (2013). Bedrock geology legend same as in Figure 2.

Williams-Jones 1991) and these minerals may be the source of elevated Ag in till and stream sediments near the deposit. Arsenopyrite is present in the deposit and in the heavy mineral fraction of metal-rich till overlying the deposit (McClenaghan *et al.* 2013*a*, 2014*a*), and is the most likely source of the highest As values in till, stream sediment and stream water.

Stream water geochemistry

Indicator/pathfinder elements in stream waters include As, Cd, Cu, Cs, W and Zn. A number of studies have demonstrated the utility of aqueous geochemistry, both ground and surface water, in geochemical mineral exploration (Leybourne *et al.* 2003; Leybourne & Cameron 2010). However few, if any, studies exist that have used water chemistry as a tool for exploration of W mineralization. Tungsten typically occurs as an oxyanion in most ground and surface waters i.e., WO_4^{2-} (i.e. most stable in its 6+ form in waters) (Baes & Mesmer 1976). There are relatively few studies of W concentrations in surface waters in general, thus it is difficult to establish background and anomalous concentrations for the Sisson area. However, in ocean waters and based on some estimates of river waters, W likely is typically on the order of tens of parts per trillion, at most. Around the Sisson deposit, proximal surface waters have dissolved W concentrations that are clearly higher than what would be considered background (i.e. hundreds of ppt rather than 10s). More detailed sampling along the streams draining the Sisson deposit would be needed to determine the potential dispersion distances of W in stream waters, but the anomalous concentrations proximal to the deposit indicate that WO_4^{2-} is a potentially powerful tool for geochemical exploration for W mineralization (Fig. 10).

Based on the elemental associations, the pathfinder elements in water include Cu, As and Mo. Aqueous dispersion of Cu will be limited by its cation form in water, which results in strong affinity for Fe- and Mn-oxyhydroxide surfaces. Conversely, W, As and Mo all form oxyanions at the pH and redox conditions typical of third and fourth order streams in New Brunswick (Leybourne *et al.* 2003), so that dispersion of these oxyanions will be greater than for the base metals (e.g., Leybourne & Cameron 2008).

Conclusions

Our research is among the first modern, commercially processed and detailed indicator mineral study of till and stream sediment around a major W deposit in glaciated terrain. Indicator mineral and geochemical methods have improved significantly over the past 30 years and are now available at a few commercial laboratories. This case study demonstrates the use of these modern methods and provides examples of signatures at varying distance down ice or downstream of s significant W–Mo deposit in glaciated terrain. The determination of the W and Mo along with a suite of elements in till, stream sediment and stream water is now routine and inexpensive.

Indicator minerals identified in the non-ferromagnetic heavy (SG > 3.2) mineral fraction of mineralized bedrock, till and stream sediment include the ore minerals scheelite, wolframite and molybdenite as well as several sulphide minerals and Bi-bearing minerals. This paper provides some of the first professional colour photographs of these small indicator mineral grains (please see online version). Of the three size fractions examined, indicator minerals are most abundant in the medium sand (0.25 – 0.5 mm) heavy mineral fraction of till and stream sediment. Indicator

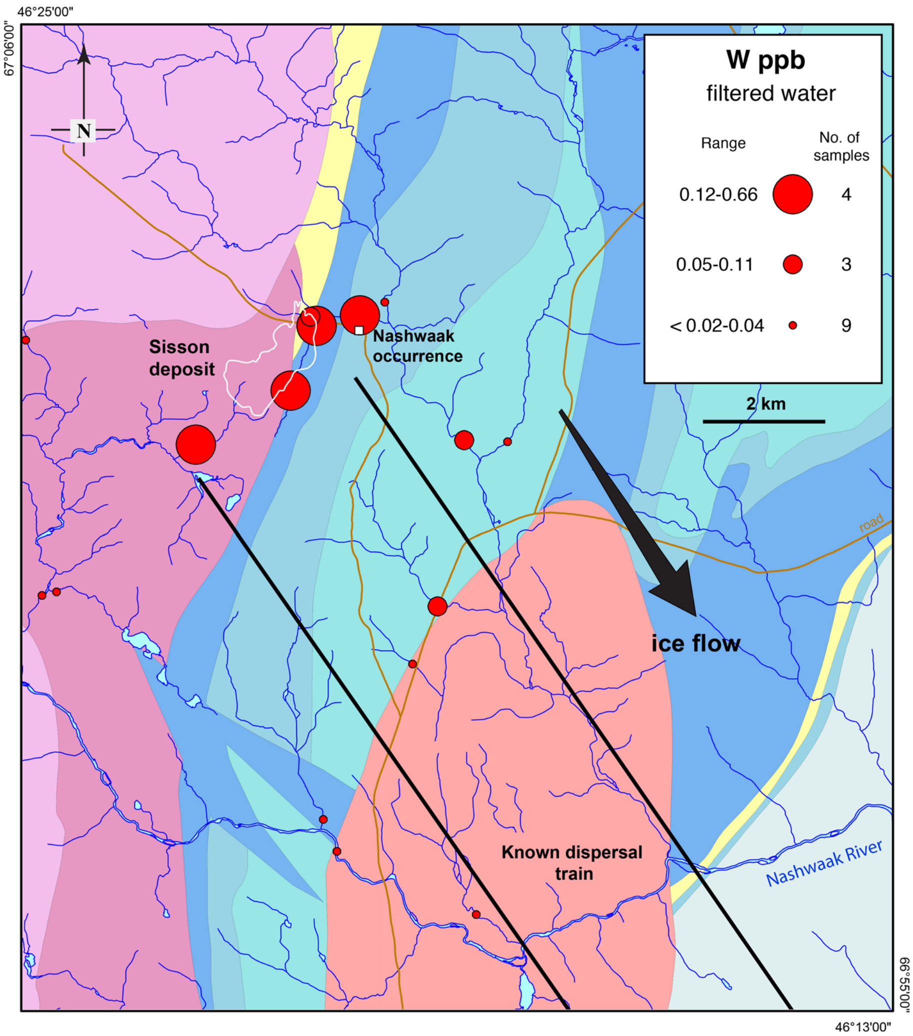

Fig. 10. Proportional dot map of W abundance in filtered stream water samples around and downstream of the Sisson deposit. Bedrock geology modified from Smith & Fyffe (2006*b*, *c*, *d*, *e*). Deposit outline in white from Rennie *et al.* (2013). Bedrock geology legend same as in Figure 2.

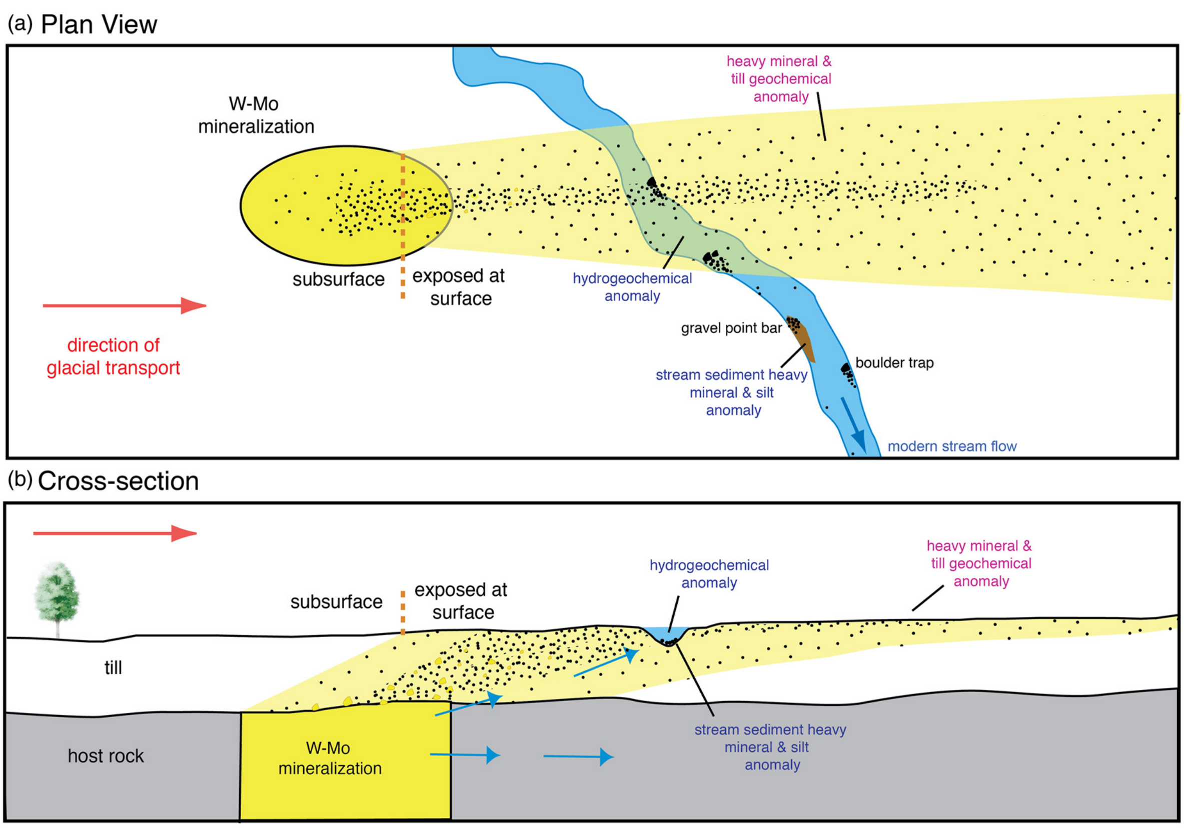

Fig. 11. Schematic plan and cross-section views of idealized clastic dispersal and chemical dispersion patterns in various media around an intrusion-hosted W–Mo deposit in glaciated terrain formed by single phase of ice flow (modified from McClenaghan & Kjarsgaard 2007).

minerals are also present in the coarse to very coarse sand (0.5 – 2.0 mm) HMC fraction of till and stream sediment samples that are proximal (<2 km) to the deposit, thus indicator mineral size can provide some insights into glacial transport distance and proximity to the bedrock source. In general, scheelite content in till decreases with increasing distance down ice (SE) of the deposit, as has been noted by Shilts (1996), DiLabio (1990), and many others for glacial dispersal from specific bedrock sources. Overlying the Sisson deposit, metal-rich till contains up to 4700 grains of scheelite, while at 1 km down ice the till contains no more than 49 grains of scheelite. Till in background areas contains 0 – 2 grains of scheelite. Fluvial dispersal of scheelite and wolframite from the deposit is detectable at least 4 km downstream from the north end of the deposit and 5 km SE of the deposit in streams that drain the SE-trending glacial dispersal train. Additional stream sediment sampling would be required to fully document the nature of dispersal of scheelite downstream from the deposit.

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 concentrates using this fluorescence is now commercially available. This method will provide consistent and comparable scheelite counts for HMC of till and stream sediment samples within, and between, projects.

Indicator mineral methods are well known for diamond and gold exploration in glaciated terrain. This case study demonstrates that indicator mineral methods have a broader application that includes W–Mo exploration, a fact that is not well known for till sampling. The W–Mo indicator minerals are part of a larger suite of indicator minerals that can be used to explore for a broad range of deposit types and commodities. This broad suite of minerals can be recovered from the same till or stream sediment sample whether the exploration target is diamonds, precious metals, base metals, strategic metals, or rare metals.

The suite of indicator/pathfinder elements in till or stream sediment is more extensive than identified in earlier geochemical studies of the Sisson deposit and region, and this reflects the polymetallic nature of the Sisson deposit as well as the broader suite of elements that is now available using modern ICP-MS and ICP-ES techniques. Few if any studies have used water chemistry as an exploration tool for W mineralization. Results presented here for stream water suggest that water chemistry, specifically W content, is a potentially powerful tool for geochemical exploration for W mineralization.

This study also identified an area of elevated Ag, As, Cu, In, Pb, Te and Zn in till as well as pyrite and spessartine in till and stream sediments overlying Ordovician rocks of the Tetagouche Group, the same package of rocks that hosts VMS deposits in the Bathurst Mining Camp. The bedrock source of the elevated metal and indicator contents overlying these rocks may be related to a distal part of the Sisson mineralizing system, or other mineralized rocks.

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