Geochemical Signatures of the South MacMillan River in the MacMillan Pass, Yukon, Including Drainages from the Tom and Jason Pb-Zn Deposits

S.E. Bryson

Department of Earth Sciences, University of Ottawa, Ottawa, ON, K1N 6N5 ed_bryson@hotmail.com

D. Fortin

Department of Earth Sciences, University of Ottawa, Ottawa, ON, K1N 6N5

M.W. McCurdy

Geological Survey of Canada, Ottawa, ON, K1A 0E8

A. Nyheim-Rivet

Department of Earth Sciences, University of Ottawa, Ottawa, ON, K1N 6N5

Abstract

During the summer of 2013, streams in the MacMillan Pass, Yukon, were sampled to characterize the stream waters of a system draining the sediment-hosted Zn-Pb (±Ag, ±Ba) Tom and Jason Pb-Zn deposits and surrounding barren shales. Streams sampled have wide ranging pH values of 2.9 to 8.2. Tributaries to the main channel are either acidic (pH <3.5), or neutral to alkaline (pH >7). Intermediate waters are found along the main channel of the South MacMillan River. Dissolved metal concentrations vary widely with water source and pH. This site is particularly interesting as streams draining the Tom and Jason deposits are acidic and neutral, respectively. The Tom deposit drainage is extremely high in dissolved and fine sediment fraction lead, as well as dissolved zinc. Neutral streams draining the Jason deposit have less dramatic metal concentrations, but do show elevated dissolved zinc and fine sediment fraction lead concentrations. This paper provides an orientation survey with signatures that an exploration geologist might expect to find downstream from a sulphide ore deposit, and indicates certain signatures which deserve further analysis before discounting a watershed as barren of ore deposits.

Recommended citation

Bryson, S.E., Fortin, D., McCurdy, M.W., and Nyheim-Rivet, A., 2015. Geochemical signatures of the South MacMillan River in the MacMillan Pass, Yukon, including drainages from the Tom and Jason Pb-Zn deposits, *in* Paradis, S., ed., Targeted Geoscience Initiative 4: sediment-hosted Zn-Pb deposits: processes and implications for exploration; Geological Survey of Canada, Open File 7838, p. 188-203. doi:10.4095/296328

Introduction

Surficial geochemical exploration methods, such as surveys performed by the Geological Survey of Canada, have a history of recorded success. Much of this success has been attributable to mechanically transported glacial drift and stream sediments (Boyle, 1979; Levson, 2001). Mechanical dispersion is limited to ore bodies exposed to surface erosion during recent geological history. In contrast, groundwater can penetrate deeply in the earth's crust and transport constituents back to the surface through dissolution, dispersion, and possible re-precipitation (Miller, 1979; Johnson, 2009). Thus, dispersion haloes created by aqueous transport have the potential to carry the geochemical signatures of ore bodies not visible in detrital sediments. While chemical weathering and mineral precipitation in stream sediments are well documented, the effect of varying environmental conditions on exploration samples are not always well understood or accounted for. Additionally, documented geochemical signatures from undisturbed ore bodies, known as orientation surveys, are limited.

Mountainous areas are particularly promising for geochemical exploration since water can interact with buried geology and resurface along a generally downward flowpath. Metal mobility, however, is extremely dependant on the properties of the water (Hermann, 1985). This becomes important for exploration since the oxidation of pyrite can generate extremely acidic, metal rich conditions known as acid rock drainage (ARD), which may or may not be related to the presence of an economic ore deposit (Kelley and Taylor, 1997; Kwong et al., 2009). Conversely, if sufficient carbonates are present within the ore body, waters may remain pH neutral with low overall metal concentrations despite the presence of economic levels of sulphide mineralization (Kwong et al., 2009). As water surfaces and enters stream flow, pH, temperature and bulk chemistry can rapidly change, limiting or enhancing the ability of elements to be carried in aqueous solution. The literature reveals few, if any, documented successes of ore bodies being located based on water chemistry alone. This limited success has not gone unnoticed and a need for method development has been a recurring theme. Refinements of existing methods have been proposed such as thermodynamic modelling of waters (Miller, 1979; Leybourne and Cameron, 2010). analysis of oxide precipitates (Carpenter et al., 1975; Huelin et al., 2006) and analysis of the suspended sediment fraction (Telmer et al., 2002). These methods attempt to measure previously dissolved metals, which have either precipitated into mineral form or adsorbed onto charged particulate material.

Clays, oxides and organics are particularly adept at adsorbing metal ions (Moore et al., 1991; Hua et al., 2012). This effect can rapidly decrease dissolved metal concentrations in stream water minimizing the size of a geochemical anomaly. Secondary metal-oxide minerals complicate inter-stream comparisons due to their susceptibility to thermodynamic conditions. As such, stream water chemistries can only meaningfully be compared to streams with similar conditions, particularly pH. Targeting highly adsorptive particles by analysing suspended sediments has the potential to both enhance the contrast of an anomaly, and increase the lateral extent of its dispersal (Telmer et al., 2002). By targeting only stream deposited fine sediments, this effect may already be visible.

The aqua regia extraction commonly used in sediment sampling programs, is a partial digestion which dissolves most base metals, sulphides, oxides, and altered silicates (Chen, 2001). Unfortunately aqua regia extractions alone do not allow for the separation of those metals contained in mechanically transported primary ore minerals (such as metal-sulphides), from those precipitated with and absorbed to oxides, clays and organics. Partial dissolution of structural silicates can also be expected to dilute the geochemical signal of an ore body with distance. Instrumental neutron activation analysis (INAA) of sediments is commonly performed by the laboratories of the Geological Survey of Canada and this is believed to represent total metal concentration including structural silicates.

In August 2013, streams in the MacMillan Pass area were sampled extensively to further the development of geochemical sampling techniques. The MacMillan Pass area provides an interesting opportunity as the Tom and Jason sediment-hosted Zn-Pb (±Ag, ±Ba) deposits are drained by acidic and neutral streams, respectively. Neighbouring streams have a wide pH range while draining no known ore deposits. In 2006, Gartner Lee performed a regional water quality, sediment and benthic invertebrate assessment of this area as a baseline study to establish water quality objectives prior to potential mining (Gartner Lee, 2007). Kwong et al. (2009) also studied selected streams in the MacMillan Pass area due to their naturally acidic properties, but no connections to mineral exploration were made. However, this site is similar to the nearby Howard's Pass, whose water were characterized for mineral exploration purposes in a Geological Survey of Canada open file (Goodfellow, 1983). Study of the acidic streams draining sedimenthosted Zn-Pb (±Ag, ±Ba) deposits of the Howard's Pass has shown Zn to be highly mobile in these environments. Conversely, Pb rapidly accumulates in sediments causing dissolved concentrations to fall significantly with distance from the metal source. In light of the three decades that have passed, it seems an opportune time to revisit this area and apply recent analytical and modelling techniques with a new orientation survey.

Site

The MacMillan Pass area is located along the south central portion of the Yukon-Northwest Territories border. It is on the eastern margin of the Selwyn Basin, an epicratonic marine basin developed during Protorozoic rifting of the North American western continental margin (Goodfellow, 2004). This rifting and associated hydrothermal activity created the Tom and Jason sediment-hosted Zn-Pb (±Ag, ±Ba) deposits Tom Zn-Pb-Ag-barite and Jason Zn-Pb-barite, are hosted in interbedded carbonaceous mudstone, diamictite, siltstone and siliceous shales of Devonian lower Earn Group rocks known as the Portrait Lake Formation (Goodfellow, 1991; Goodfellow and Rhodes, 1991). Figure 1 illustrates the regional geology relative to the sampling locations.

The site is accessed by the Canol Road, a summer access road following the valley sides. Peat-rich wetlands are common in the valley bottom, while slopes are scree covered. The South MacMillan River follows the steeply sided valley from the water divide in the MacMillan Pass for roughly 20 kilometres before entering a larger open drainage basin. Smaller tributary streams drain the surrounding mountains to the South MacMillan River at regular intervals (Figure 2).

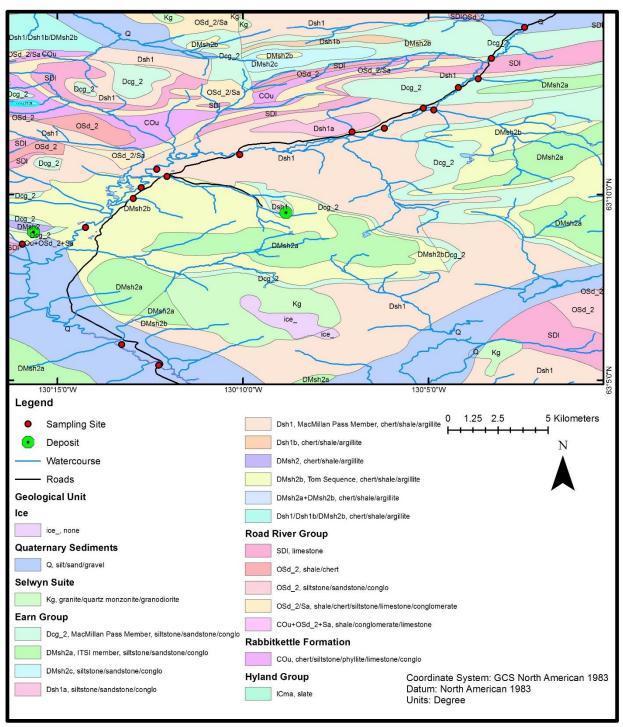


Figure 1. Geological map of the MacMillan Pass area showing stream network and sampling locations. (Modified from Gordey and Makepeace, 1999, same geological unit abbreviations used); National Topographic Data Base 105-O/1, 1990; Goodfellow and Rhodes, 1991).

Detrital stream sediments are composed of silt to boulder lag deposits. These are overlain by ferricretes in the most acidic waters (pH <3.2) (Figure 3), red Fe-oxide rich precipitates in moderately acidic waters (pH 4-5) and white Al-oxides in slightly acidic waters (pH 5-6). Neutral to basic waters without acidic tributaries have no visible precipitates.

Tributaries to the main channel are either acidic (pH <3.5), or neutral to alkaline (pH >7). The bottom of the South MacMillan River was often covered in up to a centimetre of Feoxide and Al-oxide precipitates under clear, calmly flowing regions. River reaches with faster flows suspended this finer material, clearing the river bed of all but the largest boulders and giving the waters a decidedly rusty appearance. At the Tom deposit, exploration tunnelling has been performed and untreated waters from the adit feed Seckie Creek 2. No processing is known to have occurred on site.

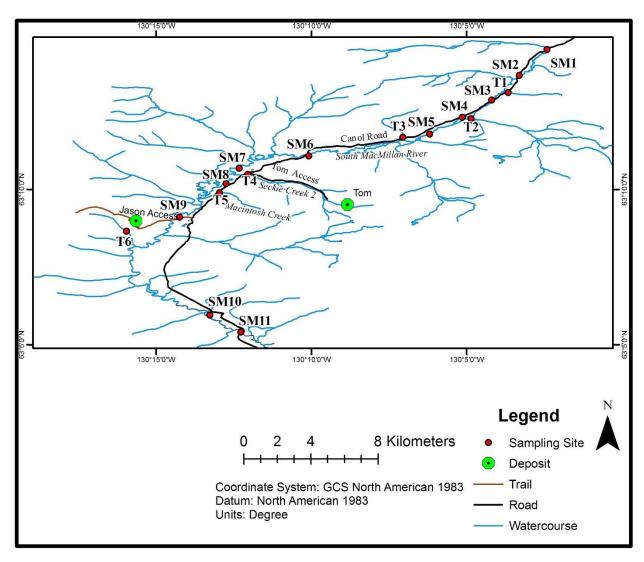


Figure 2. Site map showing sampling locations on the South MacMillan River (SM) and tributaries (T) as well as the Canol Road and Tom and Jason access roads. The South MacMillan River flows towards the bottom of the map (southwest). (Modified from the National Topographic Data Base 105-O/1, 1990).



Figure 3. A) Acidic stream (pH 3.4) at site T1 showing ferricrete stream bottom and clear waters. B) Moderately acidic stream (pH 4) at site SM5 showing heavy Fe-oxide precipitation. C) Neutral tributary at site T6 downstream of the Jason deposit showing clear waters. D) Site SM7 on the South MacMillan River with mildly acidic waters (pH 5.3) showing Al-oxide precipitation with minor Fe-oxides.

Results/Data Analysis

Methods

Sampling was performed during August, 2013 at 17 sites along the South MacMillan River and its tributary streams. Sampling and analysis followed standard Geological Survey of Canada field and laboratory procedures for stream geochemical surveys unless otherwise specified. For further information see McCurdy et al. (2012), which provides detailed field and laboratory procedures.

Where roads were in proximity to the stream or a bridge crossing is present, samples were taken immediately upstream of these locations. Water samples for dissolved cation analysis were collected mid-stream. Filtration was performed with new, 60 ml syringes rinsed with sample water through disposable 0.45 µm PAL brand filters. The initial filter discharge was used as a rinse and was not collected. Fe and Al-oxides in water courses regularly caused filter blockages and all attempts were made to change filters before excessive pressure was required to force water through the filter. Sample water was

collected in new, Environment Canada issue, 250ml, HDPE bottles, which were rinsed three times with filtered sample water. For the purposes of this analysis, 'dissolved' includes all materials passing through filtration. Samples were acidified with premeasured nitric acid (HNO₃) provided by ALS laboratories, Whitehorse, on the day of sample collection and placed into coolers. Water parameters including pH, conductivity (μS/cm), ORP (mV) and temperature (°C) were recorded on site immediately after sampling using a YSI multi-parameter meter which was calibrated daily. Samples were kept cool with ice packs and air shipped to Ottawa in these same coolers. Analysis was done by inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS) at the laboratories of the Geological Survey of Canada, Ottawa. Quality assurance was provided by three blind duplicates collected in the field, one lab duplicate, and two known standards, acid blanks and filter blanks, analysed by the laboratory. No blind standards were used. Additional sampling and field measurements were performed at these locations and analysed at the University of Ottawa for characterization of metal transport in the waters and thermodynamic modelling. These results were not finalized at the time of writing.

Stream sediment samples were collected by hand after water sampling was completed. Samples were collected at various locations over 5 to 20 m along the active stream channel in sediment sampling bags and allowed to drain and air dry on clean tarps. After being wrapped in individual plastic bags and taped shut, samples were shipped by truck to the laboratories of the Geological Survey of Canada in steel pails. Next they were dry sieved to collect the -80 mesh (<177 microns) fraction. Three splits of the fine fraction were taken with one set being stored for later use. Three blind duplicates and two known reference standards were then inserted into the other two sample splits. One sample split was sent to Becquerel Laboratories, Mississauga, Ontario, for INAA analysis providing total concentrations of 35 elements. A second sample split was sent to ACME Analytical Laboratories, Vancouver, British Columbia, for analysis by aqua regia digestion followed by inductively coupled plasma mass spectrometry (ICP-MS), providing concentrations of 65 elements. Only a subset of these elements are reported here due to space constraints. Stream precipitates were collected at some sites for analysis at the University of Ottawa with the additional water samples and the analyses were not finalized at the time of writing.

Results

Water Samples

Streams sampled had pH values ranging from 2.9 to 8.3 (Table 1) and moderate water temperatures of 8 to 14°C. The primary driver of variability was pH, with acidic (pH<4) streams having high metal loads, and neutral to basic (pH>6.9) streams having relatively low metal loads.

Many tributaries were not sampled due to time and accessibility; in at least one location the South MacMillan River appears to be significantly impacted by those tributaries that were missed. Due to mixing of tributaries, pH of the main river channel fluctuates between 3.5 and 7.1 (Figure 4). The South MacMillan River is initially acidic at site SM1 and SM2, but inputs between sites SM2 and SM3 neutralize the stream. Tributary site T2 returns

	рН	Mg	Al	Ca	Cr	Mn	Fe	Со	Ni	Cu	Zn	As	Cd	Pb
Site		ppm	ppm	ppm	ppb	ppb	ppm	ppb	ppb	ppb	ppb	ppb	ppb	ppb
LOD		0.005	0.002	0.02	0.1	0.1	0.005	0.05	0.2	0.1	0.5	0.1	0.02	0.01
SM1	3.4	4.15	10.85	18.1	0.9	444	1.2	35.3	242	69.1	914	< 0.1	10.8	0.19
SM2	4.4	4.22	7.69	18.5	0.5	334	0.5	25.7	180	50.1	679	< 0.1	7.9	0.11
T1	7.0	1.44	0.01	5.1	< 0.1	0	< 0.01	0.1	14	8.0	25	< 0.1	0.2	< 0.01
SM3	7.1	10.48	0.03	35.8	< 0.1	179	0.1	14.4	109	2.6	266	0.2	4.8	0.01
SM4	6.9	10.14	0.02	33.7	< 0.1	198	1.0	16.5	120	3.8	329	0.2	4.9	< 0.01
T2	3.3	7.95	22.14	16.9	16.9	648	24.0	68.3	435	231.0	2136	2.5	70.8	0.20
SM5	4.0	10.14	10.60	28.8	3.3	598	2.7	43.7	276	102.8	1110	< 0.1	31.4	0.08
Т3	8.3	14.34	0.06	69.6	0.2	0	< 0.01	0.1	31	8.0	21	0.4	0.7	< 0.01
SM6	4.4	13.74	8.72	28.3	1.0	678	0.4	37.1	265	80.3	1078	< 0.1	30.6	0.09
SM7	5.3	16.21	1.08	37.0	0.4	493	0.2	26.9	224	48.6	931	0.1	21.5	0.02
T4	3.0	19.69	122.16	30.5	122.5	2703	193.8	238.2	1913	507.0	14575	25.6	701.8	33.61
SM8	3.9	17.49	8.71	38.7	4.1	583	7.6	39.3	337	75.6	1759	0.4	61.5	1.55
Т5	2.9	33.42	202.53	25.0	322.5	1655	334.1	295.3	2674	305.6	7931	78.2	265.2	0.08
SM9	5.4	16.62	10.87	36.5	1.4	573	5.9	37.7	324	67.2	1634	0.2	54.0	0.63
T6	7.7	4.38	0.03	20.7	< 0.1	74	0.3	0.3	6	0.6	58	8.0	0.2	0.03
SM10	4.5	14.00	8.51	32.7	8.0	458	2.9	30.5	268	51.6	1335	0.2	42.3	0.34
SM11	4.5	12.83	6.52	30.8	0.7	432	2.4	26.6	236	45.7	1187	0.2	35.7	0.38

Table 1. Dissolved metal concentrations and pH measurements from the MacMillan Pass. Analysis performed by inductively coupled plasma emission spectroscopy (ICP-ES) for Mg, Ca and Fe; and inductively coupled plasma mass spectrometry (ICP-MS) for Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd and Pb. LOD is limit of detection.

the river to a pH of 4 by SM5. The two most acidic tributary streams, midway down the valley proximal to the Tom deposit, have a pronounced effect on the river, significantly lowering the pH. Downstream of these inputs, the main channel remains acidic and, despite reaching over 6 m wide, has a low pH of 4.5 at the most downstream sampling site. The mixing of these diverse waters causes the South MacMillan River to be extremely precipitate-rich, with red and white Fe and Al-oxide minerals visible throughout.

Metal concentrations along the South MacMillan River oscillate with the various measured and unmeasured inputs. Fe, Al, Cd, Cr, Cu, Mn, Co, Ni, Pb and Zn all show initial peaks after known acidic inputs followed by diminishing concentrations. The concentrations of Fe, Cd, and Pb in particular have large fluctuations. Ca and Mg show matching patterns; an initial increase in concentrations after the stream inputs between SM2 and SM3 followed by a generally stable trend.

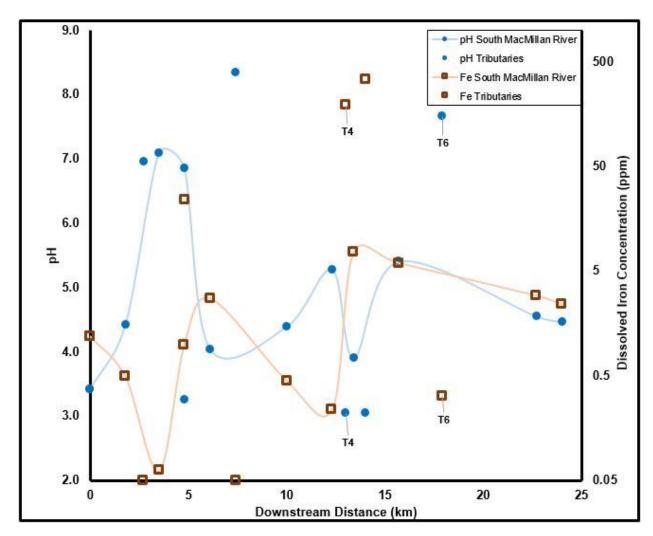


Figure 4. Highlighting the extreme variability of the study sites, this graph shows pH (left axis) and dissolved iron (right axis) with regards to distance from the most upstream site on the South MacMillan River (SM1). Sites along the South MacMillan River proper are connected while tributaries are individual point. Sites T4, draining the Tom and T6, draining the Jason deposit, are highlighted. Note that dissolved iron is plotted on a logarithmic scale.

High acidity in Macintosh Creek's waters (T5) corresponds with the highest concentrations of Al, Cr, Co, Ni, Fe, and Mg. Seckie Creek 2 (T4), draining the Tom deposit, has significantly higher concentrations of Mn, Cu, Zn, Cd and Pb. Dissolved Pb at this site is an extremely high 33.6 ppb. The only other sampling location to exceed a Pb concentration of 1 ppb was immediately downstream of the confluence of Seckie Creek 2 and the South MacMillan River.

Acidic site T2 provides an interesting contrast to Seckie Creek 2 and Macintosh Creek where, except for Cu, dissolved metal concentrations are closer to that found along the South MacMillan River. Site SM1 represents the main channel of the South MacMillan River at its headwaters. It is the only acidic tributary with no ferricrete hardpan and metal concentrations are not notably high.

Neutral to basic streams T1, T3 and T6 have by far the lowest concentrations of dissolved Mn, Co, Ni, Cd and Zn. T3 is the most basic stream sampled with a pH of 8.3. It is characterized by high Ca concentrations approaching 70 ppm. Site T1, also with neutral waters, has the lowest Ca concentration measured at just over 5 ppm.

Fine Fraction Sediment Samples

With the exception of Cr, results by aqua regia/ICP-MS analysis show similar trends to those of total sediment concentration analysis conducted by INAA. Superior detection limits, precision, and greater data set size make aqua regia/ICP-MS the preferred analytical method, which will be discussed here.

Fe concentrations are highest at T2, T4, and T5, which are underlain by Fe-oxide ferricretes (Table 2). Mn concentrations are highest at neutral drainage sites and lowest at acidic sites. Cu and Co have similar patterns to Mn, but are notably absent at site T6 and have an extreme spike at site T1. The highest Ni concentrations are found at neutral tributaries T1 and T3. The highest Al values are found at site SM7, which had extensive white Al-oxide precipitates while the lowest concentrations were acidic tributaries SM1, T2, T4, and T5. Ca and Mg are highest at the neutral upstream sites T3, SM3 and SM4.

Pb and Zn are the most notable elements in the data set. Pb's profile is characterized by an extreme spike at sampling location T4 on Seckie Creek 2, immediately downstream of the Tom deposit. While no other sediment samples exceeded 60 ppm, the concentration measured at T4 is an elevated 483 ppm. Meanwhile Zn has an extreme peak at T2, where no known ore deposit exists.

Discussion/Models

Acidic tributaries are closely associated with the Earn Group, and its geological subsets containing shales. These include the Itsi Member, Tom Sequence and Lower Earn Group. The Tom Sequence appears particularly adept at producing acidic drainages. The neutral to basic waters measured at sites SM3 and T6 have significant portions of their drainage areas underlain by the same shale bearing formations; however, both also drain areas underlain by the Road River Group, which is composed of limestone and shale (the Lower Earn Group also contains significant quantities of limestone). In the upper reaches, an un-sampled, inaccessible stream joining the South MacMillan River between sites SM2 and SM3 drains the Rabbittkettle Formation which is dominantly composed of limestone. It is notable that the stream sampled at location T1 does not appear to drain either shales or limestones, with its watershed located almost entirely within a chert pebble conglomerate known as the MacMillan Pass Member.

Characteristics of the South MacMillan River itself appear to be dominated more by mixing dynamics of the various tributary streams than interactions with the underlying geology. Downstream of major confluences, Fe-oxides rapidly precipitate, as can be seen by the dissolved Fe concentrations in Table 1 which show sharp increases at confluences followed by more gradual declines. Co, Cu, Zn, Cd, Mn and Cr show similar but more subdued patterns, likely due to their absorption to Fe and Al-oxides. The formation of Fe and Al-oxides is also acid generating, which will serve to maintain the relatively low pH values observed in the South MacMillan River along the study area.

Site	Mg	Al	Ca	Cr	Mn	Fe	Со	Ni	Cu	Zn	As	Cd	Pb
	%	%	%	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	Aqua regia/ICP-MS												
LOD	0.01	0.01	0.01	0.5	1	0.01	0.1	0.1	0.01	0.1	0.1	0.01	0.01
SM1	0.07	0.49	0.03	19.5	61	12.85	2.5	14.3	90.9	78	41.6	0.22	22.1
SM2	0.09	0.76	0.10	16.0	226	6.26	10.0	36.4	90.0	168	40.0	0.64	20.1
T1	0.13	1.46	0.17	12.7	1008	2.74	83.8	247.4	140.6	637	22.7	3.21	15.5
SM3	0.26	1.10	0.68	10.7	457	4.85	28.2	120.9	171.4	530	75.3	6.23	28.6
SM4	0.24	1.80	0.55	10.9	546	4.98	36.0	125.4	226.2	635	68.7	7.16	26.5
Т2	0.10	0.35	< 0.01	55.7	36	24.83	1.0	6.0	43.9	44	67.3	0.15	13.5
SM5	0.10	1.28	0.17	32.9	263	11.19	19.0	67.9	118.0	252	64.1	1.42	19.8
Т3	0.31	1.32	1.38	17.3	834	3.70	34.7	507.6	327.6	2354	41.0	22.01	22.0
SM6	0.09	1.29	0.15	26.2	230	7.42	12.9	59.2	118.2	250	56.7	1.36	25.6
SM7	0.09	2.86	0.32	22.1	375	5.66	19.9	97.6	219.6	486	57.4	4.36	24.4
T4	0.01	0.17	0.02	53.4	19	18.74	0.9	6.0	25.8	549	120.5	2.65	483.1
SM8	0.07	1.54	0.23	24.0	307	6.92	17.6	88.6	136.2	398	63.2	3.34	55.8
Т5	0.02	0.17	< 0.01	219.9	7	29.91	0.4	4.0	6.5	17	318.1	0.35	21.4
SM9	0.06	2.06	0.24	39.4	164	11.40	9.4	69.3	120.4	342	62.5	3.07	52.3
Т6	0.14	0.46	0.32	8.3	804	2.49	8.8	52.7	41.9	470	36.1	2.31	53.1
SM10	0.09	1.44	0.29	21.6	138	6.37	9.2	66.7	92.5	321	56.3	1.91	40.8
SM11	0.10	1.55	0.31	23.1	420	6.12	23.9	88.6	98.6	447	69.5	3.30	46.9
							INAA						
LOD	-	-	-	20	-	0.2	5	20	-	100	0.5	5	-
SM1	-	-	-	72	-	15.0	< 5	26	-	<100	50	< 5	-
SM2	-	-	-	61	-	7.8	10	40	-	170	48	< 5	-
T1	-	-	-	73	-	3.0	79	230	-	600	24	< 5	-
T2	-	-	-	71	-	32.8	< 5	< 20	-	<100	83	< 5	-
SM5	-	-	-	87	-	12.0	18	67	-	280	73	< 5	-
Т3	-	-	-	100	-	4.8	36	540	-	2400	49	21	-
SM6	-	-	-	83	-	9.2	12	68	-	270	64	< 5	-
SM7	-	-	-	79	-	6.1	20	100	-	420	61	< 5	-
T4	-	-	-	69	-	24.2	< 5	< 20	-	550	140	< 5	-
SM8	-	-	-	100	-	8.4	18	97	-	450	77	< 5	-
Т5	-	-	-	250	-	34.1	< 5	< 20	-	<100	333	< 5	-
SM9	-	-	-	80	-	12.0	10	70	-	310	65	< 5	-
Т6	-	-	-	65	-	3.1	10	54	-	440	40	< 5	-
SM10	-	-	-	79	-	7.2	7	67	-	310	61	< 5	-
SM11	-	-	-	36	-	6.4	23	70	-	360	68	< 5	-

Table 2. Metal concentrations in fine sediment fraction (-80 mesh, <177 microns) by inductively coupled plasma mass spectrometry (ICP-MS) and instrumental neutron activation analysis (INAA). Aqua regia is a partial digestion while INAA is considered to provide a complete measurement.

With regards to the Tom and Jason deposits, the waters draining each site are significantly different. The Tom deposit is drained by the acidic Seckie Creek 2, which was sampled at site T4. While this stream is highly acidic and metal rich, it is less so than the neighbouring Macintosh Creek sampled at site T5. Macintosh Creek may be geographically close to Seckie Creek 2, but it is draining a distinctly separate area from the Tom deposit itself. The extremely elevated levels of Pb in both water and sediment samples, with marginally higher Zn concentrations in the water make Seckie Creek 2 distinct from the other acidic streams (Figure 5). While the exploration disturbance to the Seckie Creek 2 drainage area may seem minimal, it is unknown whether this distinction would exist in an undisturbed watershed.

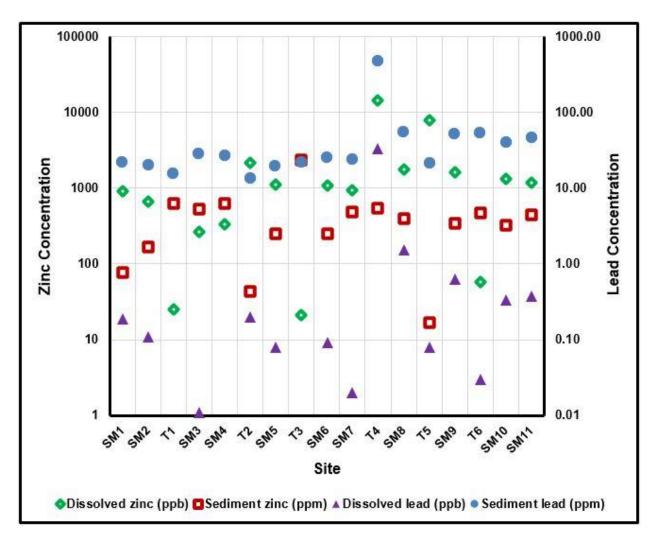


Figure 5. Zinc (left) and lead (right) concentrations in waters and sediments at various sampling sites. Sediment concentrations are those obtained by aqua regia digestion and ICP-MS analysis. Note the elevated levels of dissolved lead, dissolved zinc and sediment bound lead at site T4 downstream of the Tom deposit. The lack of sediment bound zinc at both T2 and T6 (the Jason deposit) is also notable.

The stream draining the Jason deposit sampled at site T6 also drains significant portions of the acid generating Tom Sequence; however, the carbonates occurring within the Jason deposit and the nearby Road River Group appear to neutralize any acidity initially generated. This acid neutralization also appears to have removed metals released through weathering of the Jason deposit. While the waters of this stream are somewhat distinct from waters sampled at sites T1 and T3, there is little to indicate that it is downstream of a significant ore body. In particular, Zn concentrations in the sediments are significantly lower than at the other two neutral tributaries. Pb concentrations are higher in the sediments, but it seems these alone would be inadequate to justify further exploration in this area, or even attract an individual's attention. Additionally dissolved Pb values are roughly equal to the other neutral tributary streams. Dissolved Zn concentrations are higher at T6 then at the other neutral tributary sites T1 and T3, but lower than the Zn concentrations at the two neutral sites along the South MacMillan River (SM3 and SM4). It would therefore seem unlikely that the dissolved Zn and sediment Pb values at site T6 would be enough to attract further attention.

These results are consistent with previous studies showing that Pb is guickly scavenged from the dissolved phase onto charged surfaces, and as such, is not normally found in the dissolved phase downstream of a base metal sulphide deposit. Instead, high Pb values have been commonly associated with the sediment fraction (Goodfellow, 1983). In this situation Seckie Creek 2 is close enough to the metal source for Pb to be anomalous in the dissolved fraction. Any Pb release from the Jason deposit, however, has already been scavenged and is primarily found in elevated sediment concentrations. Zinc was slightly elevated at sites downstream of ore deposits. This is again supported by studies in the Howard's Pass, where elevated dissolved and sedimentary zinc dispersal occur up to four kilometres from the ore body (Goodfellow, 1983). This is attributed to the formation of stable dissolved zinc complexes which are not readily adsorbed by surface charges on suspended materials. Unfortunately, due to its elevated mobility, Zn levels can also remain high if acidic waters draining barren shales are neutralized. The MacMillan Pass data is significant since it shows that Goodfellow's work extends beyond streams which are initially acidic to ore bodies which have acidity attenuated in situ or before the ground surface.

Implications for Exploration

It is clear that total metal concentrations alone are not enough to indicate an anomaly, as total metal loads are closely associated with acidity. However the results of this study strongly support the findings of Goodfellow in the Howards Pass district. They also partially extend his findings beyond the acidic surface waters to those neutralized before reaching the surface or *in situ*. In this situation, while the traditional analysis described readily locates the Tom deposit based on elevated Pb concentrations, it seems unlikely to have located the Jason deposit. One metal concentrations are viewed in context with pH however, the sedimentary Pb – dissolved Zn signature was significant enough to support further investigation in the region of the Jason deposit. Residual Zn from the neutralization of acidic waters also threatens to lead an exploration project astray, highlighting the importance of finding several indicators before drawing conclusions.

Perhaps most important, is the recognition that a lack of extreme metal concentrations does not necessarily indicate the absence of a base metal sulphide deposit. Subtle signatures appear more important, and may provide valuable support for findings from other techniques (such as geophysics) into a larger exploration program.

Future Work

Research is currently underway to evaluate some of the proposed refinements highlighted in the introduction. In particular, three distinct steps are underway to better characterize the waters of the South MacMillan River and its tributaries. These are: 1) analysing unfiltered water samples to determine the metal content of suspended sediment, 2) X-ray diffraction analysis of the sediments to identify the secondary mineral phases, and 3) thermodynamic modelling of the waters to determine the stable mineral phases and their relative saturation indexes. These three steps should provide more baseline data for the proposed refinements highlighted in the introduction. They may also help locate unknown sulphide deposits with subdued signatures, such as that generated by the Jason deposit.

Acknowledgements

This project would not have been possible without the timely intervention of Suzanne Paradis and Jan Peter. I would also like to thank Mark Nowosad of Yukon Energy, Mines and Resources for his incredible efforts to provide us with supplies during a period of logistical challenges. This paper is also rightfully, partially the work of Dr. James Zheng for his incredibly thorough and well researched comments during revision. This paper is greatly improved by it.

References

- Boyle, R.W., 1979, Geochemistry overview, *in* Hood, P.J., ed., Geophysics and geochemistry in the search for metallic ores: Geological Survey of Canada Economic Geology Report 31, p. 25-31.
- Carpenter, R.H., Pope, T.A., and Smith, R.L., 1975, Fe-Mn oxide coatings in stream sediment geochemical surveys: Journal of Geochemical Exploration, v. 4, p. 349-363.
- Chen, M., and Ma, L.Q., 2001, Comparison of three aqua regia digestion methods for twenty Florida soils: Soil Science Society of America Journal, v. 65, p. 491-499.
- Goodfellow, W.D., 1983, Stream sediment and water geochemistry of the Howard's Pass (XY) Zn–Pb deposit and Nor Zn–Pb–Ba occurrence, Selwyn Basin, Yukon and Northwest Territories: Geological Survey of Canada Open File 845, 27 p.
- Goodfellow, W.D., 1991, Jason stratiform Zn Pb barite deposit, Selwyn Basin, Canada [NTS 105 O 1]: Geological setting, hydrothermal facies and genesis, *in* Abbott, J.G., and Turner, R.J.W., ed., Mineral deposits of the northern Canadian Cordillera, Yukon northeastern British Columbia (field trip 14): Geological Survey of Canada Open File 2169, p. 177-191
- Goodfellow, W.D., 2004, Geology, genesis and exploration of SEDEX deposits, with emphasis on the Selwyn Basin, Canada, *in* Deb, M., and Goodfellow, W.D. ed., Sediment-hosted lead-zinc sulphide deposits: attributes and models of some major deposits of India, Australia and Canada: Narosa Publishing House, Delhi, p. 24-99
- Goodfellow, W.D., and Rhodes, D., 1991, Geological setting, geochemistry and origin of

- the Tom stratiform Zn Pb Ag barite deposits, *in* Abbott, J.G., and Turner, R.J.W., ed., Mineral Deposits of the northern Canadian Cordillera, Yukon northeastern British Columbia (field trip 14): Geological Survey of Canada Open File 2169, p. 137-175.
- Gordey, S.P., and Makepeace, A.J., compilers, 1999, Yukon bedrock geology: Geological Survey of Canada Open File 1999-1(D).
- Johnson. R.H., 2009, The influence of shallow and deep ground-water discharge on stream-water quality in a watershed with historical mining, Prospect Gulch, Colorado, USA, *in* Proceedings, International Conference on Acid Rock Drainage: 8th, Skellefteå, Sweden, 9 p.
- Hermann, R., and Neumann-Mahlkau, P., 1985, The mobility of zinc, cadmium, copper, iron, and arsenic in ground water as a function of redox potential and pH: The Science of the Total Environment, v. 43, p. 1-12.
- Hua, X., Dong, D., Liu, L., Gao, M., and Liang, D., 2012, Comparison of trace metal adsorption onto different solid materials and their chemical components in a natural aquatic environment: Applied Geochemistry, v. 27, p. 1005-1012.
- Huelin, S.R., Longerich, H.P., Wilton, D.H.C., and Fryer, B.J., 2006, The determination of trace elements in the Fe-Mn oxide coatings on pebbles using LA-ICP-MS: Journal of Geochemical Exploration, v. 91, p. 110-124.
- Kelley, K.D., and Taylor, C.D., 1997, Environmental geochemistry of shale-hosted Ag-Pb-Zn massive sulfide deposits in northwestern Alaska: natural background concentrations of metals in water from mineralized zones: Applied Geochemistry, v. 12, p. 397-409.
- Kwong, Y.T.J., Whittley, G., and Roach, P., 2009, Natural acid rock drainage associated with black shale in the Yukon Territory, Canada: Applied Geochemistry, v. 24, p. 221-231.
- Levson, V.M., 2001, Regional till geochemical surveys in the Canadian Cordillera: sample media, methods and anomaly evaluation, *in* McClenaghan, M.B., Bobrowsky, P.T., Hall, G.E.M., and Cook, S.J., ed., Drift exploration in glaciated terrain: Geological Society, London, Special Publications 185, p. 45-68.
- Leybourne, M.I., and Cameron, E.M., 2010, Groundwater in geochemical exploration: Geochemistry: Exploration, Environment, Analysis, v. 10, p. 99-118.
- McCurdy, M.W., McNeil, R.J., and Day, S.J.A., 2012, Geochemical, mineralogical and kimberlite indicator mineral data for silts, heavy mineral concentrates and waters from two geochemical surveys (2010 and 2011) on Victoria Island, Northwest Territories (NTS 87G, 87H, 88A and 88B): Geological Survey of Canada Open File 7198, 16 p.
- Miller, W.R., 1979, Application of hydrogeochemistry to the search for base metals, *in* Hood, P.J., ed., Geophysics and geochemistry in the search for metallic ores: Geological Survey of Canada Economic Geology Report 31, p. 479-487.
- Moore, J.N., Luoma, S.N., and Peters, D., 1991, Downstream effects of mine effluent on an intermontane riparian system: Canadian Journal of Fish and Aquatic Sciences, v. 48, p. 222-232.
- National Topographic Data Base 105-O/1, 1990, Department of Natural Resources, Canada Centre for Topographic Information.
- Telmer, K., Pass., H.E., and Cook, S., 2002, Combing dissolved, suspended and bed

load stream geochemistry to explore for volcanic massive sulfide deposits: Big Salmon Complex, northern British Columbia: Journal of Geochemical Exploration, v. 75, p. 107-121.