Geochemical and mineralogical controls on metal(loid) dispersion in streams and stream sediments in the Prairie Creek district, NWT

Kristina Skeries1, Heather Jamieson2*, Hendrik Falck3, Suzanne Paradis4 & Stephen Day5

Abstract: The Prairie Creek district contains several types of carbonate-hosted Zn–Pb–Ag mineralization, including stratabound replacement sulphides, quartz-carbonate-sulphide veins, and classic Mississippi Valley-type. It is located in the southern Mackenzie Mountains of northwestern Canada and within the boundaries of Nahanni National Park Reserve. The Prairie Creek district does not produce a strong geochemical signal in comparison to other mineralized areas of similar deposit types. Stream waters and sediments draining the district were sampled to determine the concentrations of Pb, Zn, Ag, As, Cd, Cu, Hg, Sb, and Se, and to investigate the minerals hosting these elements, to investigate the geochemical controls on the mobility of these elements and any trends in dispersion. Results indicate that Zn and Pb are the most useful pathfinder elements, with anomalous concentrations in water downstream from Mississippi-Valley type mineralization and in sediments downstream from quartz-carbonate-sulphide vein mineralization. Zinc is more mobile than Pb, but elevated concentrations of neither element persist downstream of the metal source. Microanalytical examination of silt sediments indicate that Zn and Pb are associated with goethite and hematite, confirming active chemical weathering in this subarctic alpine environment.

Keywords: Zn-Pb-Ag mineralization; stream water; stream sediment; pathfinder elements; microanalysis; chemical weathering; Nahanni National Park

Received 1 June 2015; revised 5 August 2016; accepted 29 October 2016

The Prairie Creek carbonate-hosted Zn–Pb–Ag deposits are located approximately 500 km west of Yellowknife in the Mackenzie Mountains of the Northwest Territories, Canada. The recent expansion of the Nahanni National Park Reserve means that the property, which current owners plan to bring into production, now occupies a 320 km² enclave entirely surrounded by the Park and property, which current owners plan to bring into production, now

The Prairie Creek district contains several types of carbonate-hosted mineralization (Fig. 2a), including stratabound replacement massive sulphides (SMS), quartz-carbonate-sulphide veins, and Mississippi-Valley type (MVT) or cavity-infill type (Paradis 2007, 2015). The SMS and quartz-carbonate-sulphide veins have been extensively explored and represent the currently defined mineral resources, which totalled 7.6 million tonnes of proven and probable reserves at a combined grade of 17% Pb and Zn and 128 grams/tonnes Ag (AMC Mining Consultants (Canada) Ltd. 2016).

Previous investigations of stream water and sediment geochronology in the district have shown that although mineralization in this area can be detected, the geochemical signals tend to be rather muted and do not persist to a distance sufficient for vectoring purposes (i.e. tracing the signal back towards the deposit) (McCurdy et al. 2007).

This study investigates the geochemical signature of the Prairie Creek quartz-carbonate-sulphide vein and MVT deposits and aims to identify key processes occurring in the stream sediments and waters by analysing chemical and mineralogical data downstream from known mineralization of various types. Mineralogical characterization using microanalytical techniques has been used to identify minerals that are leaching metals and precipitating or attenuating them. The pathfinder elements chosen include Pb, Zn, Ag, As, Cd, Cu, Hg, Sb, and Se, as these are typically used in geochemical surveys associated with similar types of deposits, and they have been found in elevated concentrations in previous water studies (Phase Geochemistry 2010). The results are applicable not only to the improved understanding of element vectors for Pb–Zn–Ag deposits in carbonate rocks, but provide baseline information relevant to the subarctic alpine environment.

Geology and Mineralization

The deposits at Prairie Creek (Fig. 2a) are hosted by Lower Paleozoic sedimentary rocks such as limestone, dolostone, and shale of the Prairie Creek Embayment (Morrow & Cook 1987). These rocks represent a transitional sequence between the shelf carbonates of the Mackenzie platform and the basinal shales of the Root Basin. Following deposition of the sedimentary strata, the Prairie Creek Embayment underwent deformation, due to the collision between the western margin of the North American craton and an island arc system. The three-phase deformation event resulted in doubly-plunging, faulted anticlines, broad, flat-bottomed synclines, steeply dipping reverse faults, and flatter thrust faults (Morrow & Cook 1987; Falck et al. 2007).

The sulphides are hosted within the quartz-carbonate-sulphide vein system defined by fractures running parallel and sub-parallel to major regional north–south (N–S) structures. The veins are expressed discontinuously in twelve exposures along a N–S-trending 16 km-long corridor, including the Prairie Creek mine site where MQV is exposed in underground workings (Paradis 2007). The MQV is associated with a north-striking, steeply east dipping, near-vertical fault. It has a width of 2–3 m, and a strike length of at least 2.1 km. Drill hole intercepts suggests the vein extends to at

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least 600 m below surface (Canadian Zinc Corporation 2010). The quartz-carbonate-sulphide vein mineralization crosscuts several formations – most notably, the dolostones of the Whittaker Formation, the shales of the Road River Formation, the thinly-beded limy shales of the Cadillac Formation, the cherty siltstones of the Arnica Formation, and the dolostones of the Root River Formation. The main sulphides are sphalerite and galena with lesser concentrations of tetrahedrite-tennantite and pyrite (Paradis 2007). The gangue minerals are quartz, calcite, and dolomite.

The stratabound replacement sulphides do not outcrop, and have been located by drilling in four zones proximal to the mine site. The sulphides form several lenses that replaced the host dolostones of the Upper Whittaker Formation, consisting of pyrite, sphalerite, galena and trace amounts of tetrahedrite-tennantite in a gangue of quartz, dolomite, and calcite (Paradis 2007).

The Mississippi Valley-type occurrences (e.g. Samantha, Road, Zebra) are exposed on the ridges NE of the Prairie Creek mine site and they are hosted by the light grey dolostone of the Root River Formation (Paradis 2007). They consist of pyrite, sphalerite, and minor galena that fill open spaces and fractures in the dolostone.

Lead, zinc and silver are the main commodities of the Prairie Creek Mine, with appreciable amounts of copper. The main sulphide minerals in the stratabound and vein systems are galena, sphalerite, and minor tennantite-tetrahedrite and pyrite, whereas in the MVT occurrences the sulphides are mainly pyrite and sphalerite with rare galena. The upper portion of the sulphide vein system has undergone oxidation, and the ore-bearing minerals have been predominantly altered to smithsonite (ZnCO₃), cerussite (PbCO₃), malachite (Cu₂CO₃(OH)₂) and azurite (Cu₃(CO₃)₂(OH)₂) (Paradis 2007, 2015; Stavinga et al., in press). The oxidized portion of the vein is likely a result of the circulation of oxygenated meteoric and ground waters that altered the sulphides and remobilized the metals from the sulphides to the adjacent host rock (MESH Environmental Inc. 2008; Paradis 2015).

The current climate at Prairie Creek is generally subarctic, and considered to be of Dfc type (D = Cold; f = without dry season; c = cold summer) under the Köppen-Geiger climate classification system (Peel et al. 2007). This classification is based on the mean temperatures of the hottest and coldest months, along with the precipitation of the driest month in summer and driest month in winter. There is evidence suggesting that the area was not covered by the Laurentide ice sheet in the Pleistocene (Duk-Rodkin et al. 2007), although it was likely influenced by meltwaters, as evidenced by the presence of rare granite boulders which have no nearby sources.

Field Sampling

Samples of stream water and sediments were collected in July–August 2011 from thirty-six sites along six streams (Fig. 2a and b, red circles). Locations were chosen to compliment the previous sampling efforts by the MERA program (Fig. 2a and b, green circles, please see online version for colour figure), but were also chosen to be proximal to known outcrops of sulphide mineralization. Samples were collected from streams ranging from steeply dipping and steeply banked, to rather flat and wide. Furthermore, streams selected for sampling locations were also chosen that represented varying degrees of anthropogenic disturbance (for example, Rigor Mortis Creek represented the least disturbed, whereas Harrison Creek represented the most disturbed). Where possible, samples were taken every 250 m upstream and downstream of known quartz-carbonate-sulphide vein and MVT showings.

Specifically, all sample locations were downstream of quartz-carbonate-sulphide vein showings in Rigor Mortis Creek, though veins were present downstream as well (Fig. 3a). All sample locations were downstream of MVT showings in Funeral Creek (four of these samples are also upstream of quartz-carbonate-sulphide vein showings), and two sample locations were downstream of quartz-carbonate-sulphide vein showings in Funeral Creek (Fig. 3b). Two sample locations were upstream, and one sample location was downstream, of quartz-carbonate-sulphide vein showings in Prairie Creek, as well as the mine site and confluence with Harrison Creek. In Harrison Creek, nine sample
locations were upstream of quartz-carbonate-sulphide vein showings, and two were taken downstream.

Sample collection generally followed procedures outlined in Friske & Hornbrook (1991). At each site, water samples were collected mid channel from flowing water into triple rinsed Nalgene HDPE bottles. Single-use Millipore Sterivex-HV 0.45 μm syringe filter units were used onsite for the filtered samples. Within 24 h of collection, samples requiring acidification were acidified with 8 M ultrapure nitric acid. *In situ* measurements of water temperature, pH, conductivity, and oxidation-reduction potential were made using a YSI multiprobe.

Fig. 2. Geology and sampling locations of the Prairie Creek Mine area. Red circles represent the study sampling locations; green circles represent previous sampling studies of the MERA program. Quartz-carbonate-sulphide vein showings are represented by purple squares, and MVT showings are represented by light green triangles.
Dissolved oxygen values were recorded with a different YSI multiprobe upon returning to the mine facilities. All meters were calibrated on a daily basis prior to sampling. Filter blanks, acid blanks, and travel blanks were also taken. Four of each blank type was produced over the length of the field season. All water samples were stored in coolers in the dark and at temperatures between 2 and 3°C. Stream sediment samples consisted of silt and fine grained sand collected from the active stream bed (Friske & Hornbrook 1991). At 8 sites, sediment was scarce or absent and a moss mat sample was collected instead. Previous studies (Gravel et al. 2008) have shown that, for most elements, moss mat results are similar to those from fine-grained sediments. Collection of sediment samples was always taken either downstream from, or following, water sample collection to avoid contamination of the water samples. For 12 sites, an additional sample was collected from the coarse sediment fraction and was taken, usually at high-energy, upstream points of mid-channel bars, and wet-sieved on site to <1.68 mm.

**Analytical Methods**

Water samples were analysed by the Inorganic Geochemistry Research Laboratory at Natural Resources Canada, using ICP-MS (Inductively Coupled Plasma Mass Spectrometer) and ICP-ES (Inductively Coupled Plasma Emission Spectrometer) for analysis of cations, and using a Dionex ACS 2100 Ion Chromatography for analysis of anions. Dissolved organic carbon was determined using a Shimadzu 5050 TOC analyzer.

Stream sediment samples were sieved to <177 μm and analyzed by ICP-MS/ICP-ES (Acme Analytical Laboratories (Vancouver) Limited) for 53 elements after aqua regia digestion. Fluoride was analyzed by ion selective electrode (ISE). Total carbon, inorganic carbon, organic carbon, and loss on ignition were also determined. Analysis by ICP-MA/ICP-ES following digestion using a 4-acid solution was also conducted. Multiple analytical methods were used to be consistent with a previous regional geochemical survey (McCurdy et al. 2007).

The coarse mineral fraction (<1.68 mm) underwent heavy mineral concentrate analysis at Overburden Drilling Management (Ottawa). This involves a combination of gravity separation, heavy liquid separation, and magnetic separation, as well as grain counts of targeted minerals (McClennan 2007). The heavy, non-magnetic fraction of <0.25 mm were analysed for 54 elements by ICP-MS/ICP-ES, after aqua regia digestion as described in Falck et al. (2012).

Spearman correlation matrices were produced using ioGas™ (©ioAnalytics Pty Ltd) for water and sediment analyses, incorporating data from previously completed surveys (McCurdy et al. 2007) to increase sample populations for statistical analysis. To identify anomalies, a combination of median normalization and a variation on weighted-sums was used. First, a standardization of the concentrations of the elements of interest, in both the stream sediments and stream water samples was performed. After consideration of the distribution shape for elemental concentrations, it was decided that using the median as a measure of central tendency would provide more representative results, as the distributions were skewed and there were often very distinct populations. The median is also more resistive to anomalous values, whereas the mean is heavily influenced by outliers (Reimann et al. 2008). To normalize the values, the median concentration was determined for each element, and each result was then divided by its respective median value. This expresses the concentrations in multiples of the median, effectively allowing for quick discrimination of anomalies, as any result greater than the 50th percentile has a value of greater than 1. The use of median-normalized score values ensured that any anomalies retained their relative weight in the sum, even if their true concentrations are below the background concentrations of the other elements, or seemingly not anomalous. This also ensured that high detection limits were not mistaken for anomalous values. This method of using median-normalized values has also been used in the previous MERA study (McCurdy et al. 2007).

Following median-normalization, the elements of interest were summed for each sample location. The method of weighted sums has been developed and used for exploration geochemistry purposes (Garrett & Grunsky 2001), often using values for the elements that are based on a score between 0 and 3. These scores are assigned to the median-normalized values based on the degree of anomaly (Chaffee 1983). In this case, to enable greater distinction of anomalous results, the median normalized values were not scored prior to summing and were then plotted as a percentile of the entire range of resulting sums. This allowed for a finer detail to be mapped, which was deemed necessary as it was known prior to the study that the geochemical signature of the mineral showings would be relatively weak.

The summed values were converted to percentile and binned using the progressive half method in ioGas™ (©ioAnalytics Pty Ltd). The percentile value for each sample location was then plotted using ioGas™ (©ioAnalytics Pty Ltd) coupled with Esri® ArcGIS™. The resulting map indicated general trends of dispersion along the different types of mineralization, while taking all elements of interest into account.

The proportion of contribution by each element of interest to the sum for each sample location was determined by dividing the median-normalized score value of each individual element of...
interest by the sum of the elements of interest. When these proportions for each element of interest are taken into account across the region, the result indicates which elements are the most anomalous contributors with respect to the region and the extent of the survey and not just the greatest absolute concentration for each location.

Thin sections were made of six stream sediment samples with the highest concentrations of the elements of interest. Characterization was accomplished using optical microscopy, scanning electron microscope (SEM, Quanta 650 FEG-ESEM), electron microprobe (JEOL JXA-8230), and synchrotron-based micro X-ray diffraction (μ-XRD) and micro X-ray fluorescence (μ-XRF). Synchrotron microanalysis employed methods reported previously (Walker et al. 2009, 2011). Polished thin sections were lifted from the glass slides using HPLC-grade acetone and carefully placed on polyimide (Kapton) tape. Element mapping using μXRF was performed at a beam energy of 13 500 eV, while μXRD was performed at 17 479 eV. Beam spot size is approximately 6 by 9 μm, and micro-XRF maps were produced with a step (pixel) size of 5 μm, and a dwell time of 0.1 – 0.3 seconds/pixel, depending on the area being mapped. Micro-XRD was imaged with a Bruker SMART 1500 CCD detector. The detector was calibrated using overlaid patterns of silver behenate and α-Al2O3 (SRM 674a).

The element maps produced by μXRF provide qualitative element associations that assist in constraining the XRD fits, and element associations for particles when no or poor diffraction is observed. Diffraction patterns from the μXRD were converted to 2D spectra using Fit2D™ (Hammersley 2004). Both conventional and micro-XRD 2D spectra were fitted to mineralogical phases using the peak-matching software X-Pert HighScore Plus (PANalytical) and the most recent mineral library. Each unknown pattern was background minimized by scaled subtraction of blank XRD patterns collected on Ultralene over acrylic polyimide tape. Corrections for detector distortions (camera-sample distance, the camera tilt and rotation, and the beam center on the camera plane) were made using Fit2D software (Hammersley 2004). Unknown patterns were identified by masking all point

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Fig. 4. Variation in alkalinity, conductivity and element concentrations with distance for streams sampled in the Prairie Creek area: (a) Rigor Mortis (b) Funeral (c) Harrison (d) Prairie creeks. Dotted lines represent possible interaction with mineralized showings.
reflections, importing into X-Pert High-Score software Version 2.2a (PANalytical) for conventional search-match phase identification using the PDF2 database.

Approximately 40 target grains with representative or unusual texture or chemical signature were analysed. These were either pre-selected based on SEM examination or identified from element maps.

**Results**

**Water and Sediment Analyses**

Figure 4a-d display selected filtered water and sediments results from the four major streams sampled. Parameters measured but not reported here include pH (which varied between 8.2 and 8.6), ORP (43 – 224 mV), dissolved oxygen (DO) (9.5 – 12 mg/L), major cations and anions, and metals in water and major elements and metals in sediments (Skeries 2013).

**Rigor Mortis Creek**

Samples from Rigor Mortis Creek (Fig. 4a) show probable interaction with vein mineralization. Although no known showings of the quartz-carbonate-sulphide vein occur directly adjacent to the stream, there are showings located less than 1 km from the first sample point both directly north and directly south of the stream. These showings are within the catchment area for Rigor Mortis Creek (Canadian Zinc Corporation 2010). Both the Prairie Creek fault and the trace of the quartz-carbonate-sulphide vein are seen to intersect Rigor Mortis Creek prior to the first sample point. In the stream sediments, all metal concentrations (As, Cu, Cd, Pb, Sb, Zn, Ag, Hg and Se) increase in the first 250 m of the stream bed (first two sample points). In the water, Pb, Cd and Sb increase over the same interval. Conductivity and alkalinity increase over the length of the stream, and pH shows an increase from 7.5 to 8.2. This may reflect dissolution of carbonate minerals as suggested by increases in dissolved Ca.
(from 69 to 91 mg/L) and Mg (from 23 to 44 mg/L) in the water samples (Skeries 2013).

**Funeral Creek**

Funeral Creek (Fig. 4b) shows input from both the Mississippi-Valley type mineralization at the headwaters (e.g. Road and Zebra showings), and the quartz-carbonate-sulphide vein mineralization between sample points located at 2.4 and 3.7 km from the first sampling location. Zinc and Cd are highest in the first two samples for both sediment and filtered water, probably influenced by the MVT mineralization. This pattern is also seen for Cu, Pb, and Ag in unfiltered water (Skeries 2013), but does not appear for filtered water, reflecting the influence of suspended particles. The quartz-carbonate-sulphide vein mineralization appears to impact stream water (increases in As and Sb) and sediment (increases in As, Sb, Cu, Hg and Pb). Zinc exhibits only a slight increase downstream of the vein mineralization, whereas Cd shows a marginal increase immediately following the vein mineralization, but decreases downstream. Conductivity and alkalinity increase slightly, consistent with increases in Ca (from 25 to 41 mg/L) and Mg (from 14 to 20 mg/L) (Skeries 2013), while pH showed a decrease from 8.2 to 6.7.

**Harrison Creek**

Harrison Creek (Fig. 4c) results are much more variable than Rigor Mortis Creek, and interaction with sulphide mineralization is not as apparent. It is difficult to separate the geochemical signal resulting from mineralization from that which can be attributed to anthropogenic disturbance (the mine site). Showings and bedrock mapping indicate that the projection of the vein at depth crosses Harrison Creek at, or immediately before, the confluence with Prairie Creek (Canadian Zinc Corporation 2010). Most of the elements of interest show a general decrease in concentration over the sampling length, before becoming more elevated at the sample site located 2.5 km from the first sampling location. The 2.5 km site is in the area of where the vein is projected to be exposed but it is
also where treated mine water is released to Harrison Creek, and it is difficult to distinguish the magnitude of the effect each source has on the resulting stream chemistry. These results are consistent with previous water analyses of Harrison Creek (Canadian Zinc Corporation 2010), which also identified the trend of increased metal concentrations in the area of the mine and the mine discharge. This was primarily attributed to the mine discharge, but the possibilities of runoff from existing waste rock piles and the contribution of metal-enriched groundwater due to interaction with mineralization were also discussed.

The increase of metal concentrations towards the confluence with Prairie Creek is more pronounced in the stream sediments than the water. Zinc concentrations in the water increase over a short distance to 258 ppb at the last sample site which is at the confluence of Harrison and Prairie creeks (Fig. 4c). Conductivity and alkalinity increase over the length of the stream, which is consistent with a general increase in Ca and Mg over the length of the stream; pH remains fairly consistent, ranging from 8.1 to 8.6.

**Prairie Creek**

Three locations were sampled along Prairie Creek (Fig. 4d), a relatively large stream that bisects the property over a distance of approximately 18 km and runs directly beside the mine site. Two sample locations were established upstream of the mine site and a third sample location was established downstream of the mine site. Alkalinity and conductivity along Prairie Creek vary little, but do show a slight decrease and subsequent increase (pH increases at a consistent rate from 8.3 to 8.5 over sampled length of the stream). In the stream water, concentrations of all elements of interest, with the exception of Cu, decrease before increasing between the second and third sample locations. Copper shows an increase before a subsequent decrease between the second and third sample points. In the stream sediments, all elements of interest show a decrease in concentration between the second and third sample points; however, only Cu, Hg, and Pb show increases in concentrations prior to the second sampling location, while the remaining elements of interest decrease. The confluence of Prairie Creek and Harrison Creek,
Table 1. Spearman correlation matrix of selected parameters and elements, for stream sediments digested by aqua regia and analyzed by ICP-MS/ES (n = 96)

| Parameter | Alkalinity (ppm CaCO₃) | Conductivity (uS/cm) | pH | DO | Eh | LOI (%) | Ag (ppb) | As (ppm) | Cd (ppm) | Cu (ppm) | Hg (ppb) | Pb (ppm) | Sb (ppm) | Se (ppm) | Zn (ppm) |
|-----------|------------------------|----------------------|----|----|----|---------|-----------|----------|----------|----------|----------|----------|---------|---------|---------|---------|
| Alkalinity (ppm CaCO₃) | 1                      |                      | 1  |    |    |         |           |          |          |          |          |          |         |         |         |         |
| Conductivity (uS/cm)     | 0.9                   | 1                    |    |    |    |         |           |          |          |          |          |          |         |         |         |         |
| pH                     | 0.59                  | 0.28                 | 1  |    |    |         |           |          |          |          |          |          |         |         |         |         |
| DO                     | −0.12                 | −0.082               | −0.19 | 1 |    |         |           |          |          |          |          |          |         |         |         |         |
| Eh                     | −0.41                 | −0.35                | −0.24 | −0.09 | 1 |         |           |          |          |          |          |          |         |         |         |         |
| LOI (%)                | 0.65                  | 0.63                 | 0.29 | 0.065 | −0.033 | 1 |         |           |          |          |          |          |          |         |         |         |         |
| Ag (ppb)               | 0.55                  | 0.43                 | 0.21 | −0.11 | −0.16 | 0.71 | 1         |           |          |          |          |          |          |         |         |         |         |
| As (ppm)               | 0.7                   | 0.62                 | 0.13 | 0.12 | −0.08 | 0.85 | 0.81 | 1         |           |          |          |          |          |          |         |         |         |
| Cd (ppm)               | 0.15                  | 0.091                | 0.18 | 0.14 | −0.0067 | 0.29 | 0.78 | 0.55 | 1         |           |          |          |          |          |          |         |         |
| Cu (ppm)               | 0.68                  | 0.58                 | 0.078 | −0.13 | −0.079 | 0.87 | 0.79 | 0.86 | 0.51 | 1         |           |          |          |          |          |          |         |
| Hg (ppb)               | 0.52                  | 0.47                 | 0.29 | −0.22 | −0.16 | 0.71 | 0.87 | 0.68 | 0.65 | 0.66 | 1         |           |          |          |          |          |          |
| Pb (ppm)               | 0.2                   | 0.18                 | 0.27 | −0.17 | −0.038 | 0.37 | 0.77 | 0.54 | 0.66 | 0.52 | 0.79 | 1         |           |          |          |          |          |
| Sb (ppm)               | 0.69                  | 0.65                 | 0.21 | −0.17 | −0.14 | 0.78 | 0.88 | 0.84 | 0.66 | 0.84 | 0.82 | 0.63 | 1         |           |          |          |
| Se (ppm)               | 0.63                  | 0.45                 | −0.13 | 0.041 | 0.023 | 0.91 | 0.64 | 0.77 | 0.52 | 0.74 | 0.49 | 0.3 | 0.72 | 1         |           |          |
| Zn (ppm)               | −0.017                | −0.067               | 0.14 | 0.096 | −0.031 | 0.13 | 0.7 | 0.47 | 0.93 | 0.44 | 0.64 | 0.73 | 0.58 | 0.42 | 1         |           |
| Al (%)                 | 0.37                  | 0.29                 | −0.17 | −0.12 | −0.032 | 0.56 | −0.017 | 0.12 | −0.24 | 0.32 | 0.019 | −0.11 | 0.085 | 0.1 | −0.16 | 1         |
| Ca (%)                 | −0.41                 | −0.42                | −0.12 | 0.023 | 0.077 | −0.79 | −0.7 | −0.64 | −0.53 | −0.71 | −0.58 | −0.37 | −0.71 | −0.61 | −0.46 |         |
| Fe (%)                 | 0.47                  | 0.2                  | −0.12 | 0.34 | −0.069 | 0.44 | 0.19 | 0.34 | 0.11 | 0.46 | 0.0018 | 0.04 | 0.1 | 0.25 | 0.086 |         |
| K (%)                  | 0.62                  | 0.51                 | −0.11 | −0.37 | −0.06 | 0.7 | 0.19 | 0.32 | −0.021 | 0.47 | 0.16 | 0.043 | 0.36 | 0.4 | −0.0038 |         |
| Mg (%)                 | −0.63                 | −0.4                 | 0.15 | −0.036 | 0.11 | −0.71 | −0.0095 | 0.26 | 0.13 | −0.39 | 0.074 | 0.3 | −0.099 | −0.33 | 0.25 |         |
| Na (%)                 | −0.79                 | −0.68                | −0.13 | 0.3 | −0.83 | −0.57 | −0.65 | −0.29 | −0.73 | −0.51 | −0.24 | −0.68 | −0.59 | −0.18 |         |         |
| P (%)                  | 0.58                  | 0.59                 | −0.052 | −0.0042 | 0.0088 | 0.89 | 0.54 | 0.66 | 0.29 | 0.64 | 0.51 | 0.3 | 0.67 | 0.69 | 0.21 |         |
| S (%)                  | 0.42                  | 0.047                | 0.099 | −0.23 | −0.42 | −3.9E+17 | −0.17 | −0.26 | −0.2 | 0.0009 | −0.28 | −0.2 | −0.22 | −0.08 | −0.19 |         |

Alkalinity (ppm CaCO₃)
Conductivity (uS/cm)

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<th>Parameter</th>
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</table>

Bold values indicated correlation coefficients >0.5 or <−0.5. Positive numbers indicate positive correlations; negative numbers indicate negative correlations.
which receives treated mine water, occurs between the second and third sample points in Prairie Creek, and may contribute load to Prairie Creek. Also of note is that the water sample may have been influenced the vein exposure along the bank of Prairie Creek, or a spring located between the mine and the sample site (Caron et al. 2008). In general, metal concentrations in the water show a decrease and subsequent increase, while stream sediments vary in between the first and second sample point, but all elements of interest show a decrease between the second and third sample points.

**Moss Mat Samples**

Some sediment samples from Rigor Mortis Creek (at 0.3 and 1.0 km from the first sampling location) and Harrison Creek (0.8, 1.1, 1.4, and 1.9 km from the first sampling location) were extracted from moss mats. A slight increase in Hg concentrations in those samples is much less than the variation associated with the intersection of vein mineralization. The Hg may only be responding with enhanced concentrations in moss mats as per the results of Gravel et al. (2008).

**Coarse Sediment Fraction and Heavy Mineral Concentrate**

Metal content in the heavy mineral concentrate of the coarse fraction of the sediments is elevated relative to the corresponding silts as a product of the concentrating effect of the separation based on density and magnetic properties (McClenaghan 2011). The heavy mineral analyses showed that barite is the major heavy mineral, followed by pyrite, sphalerite and galena. Malachite, chalcopyrite and smithsonite were present as trace amounts. Anomalously elevated proportions of sphalerite and galena (60 and 20% of the total heavy mineral count, respectively) were observed in the sediment sample taken at the site in Harrison Creek 2.5 km from the top site, which may have been influenced by vein mineralization or anthropogenic disturbance (Fig. 4c).

**Statistical Analyses**

Correlation matrices for stream silt sediments (Table 1) show strong correlations ($r_s = 0.7$) for Zn–Cd ($r_s = 0.93$), Ag–Sb ($r_s = 0.88$), Ag–Hg ($r_s = 0.87$), As–Cu ($r_s = 0.86$), As–Sb and Cu–Sb (both $r_s = 0.84$), Hg–Sb ($r_s = 0.82$), Ag–As ($r_s = 0.81$), Ag–Cu and Hg–Pb (both $r_s = 0.79$), Ag–Cd ($r_s = 0.78$), Ag–Pb and As–Se (both $r_s = 0.77$), Cu–Sb ($r_s = 0.74$), Pb–Zn ($r_s = 0.73$), Sb–Se ($r_s = 0.72$), and Ag–Zn ($r_s = 0.7$). There were no strong correlations between the trace elements of interest and the major elements (Al, Ca, Fe, K, Mg, Na, P, S).

Heavy metal concentrate samples show strong correlations ($r_s = 0.7$) for Hg–Ag ($r_s = 0.95$), Pb–Cd ($r_s = 0.92$), Cu–Sb ($r_s = 0.91$), Cu–As ($r_s = 0.87$), Hg–Pb, Hg–Cd, and As–Sb (all $r_s = 0.84$), Ag–Pb ($r_s = 0.81$), Zn–Cd ($r_s = 0.80$), Se–As, Se–Cu, and Se–Sb (all $r_s = 0.79$), Ag–Cd ($r_s = 0.76$), and Ag–Sb ($r_s = 0.75$) (Table 2). The only strong correlation between the trace elements of interest and the major elements was that between Se and P ($r_s = 0.81$).

Summed, median-normalized score values showed distinct differences between the stream sediment and the water concentrations. Figure 5 shows the summed values as percentiles for each method of analysis (see Fig. 5a for filtered water results and Fig. 5b for stream sediment results). These maps highlight the difference in the geochemical signature of the different sampling media according to the type of mineralization that is potentially influencing the concentrations. The stream sediments show higher percentile summed values surrounding quartz-carbonate-sulphide vein mineralization, while the filtered water samples show higher percentile summed values within proximity of the MVT mineralization.

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### Table 1. Spearman correlation matrix for major parameters and elements, for heavy mineral concentrates ($n = 12$)

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Ca</th>
<th>Fe</th>
<th>Mg</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1</td>
<td>0.2</td>
<td>0.76</td>
<td>0.45</td>
<td>0.87</td>
<td>0.32</td>
</tr>
<tr>
<td>Ca</td>
<td>0.2</td>
<td>1</td>
<td>0.54</td>
<td>0.54</td>
<td>0.85</td>
<td>0.45</td>
</tr>
<tr>
<td>Fe</td>
<td>0.76</td>
<td>0.54</td>
<td>1</td>
<td>0.33</td>
<td>0.35</td>
<td>0.85</td>
</tr>
<tr>
<td>Mg</td>
<td>0.45</td>
<td>0.54</td>
<td>0.33</td>
<td>1</td>
<td>0.85</td>
<td>0.73</td>
</tr>
<tr>
<td>P</td>
<td>0.87</td>
<td>0.85</td>
<td>0.35</td>
<td>0.85</td>
<td>1</td>
<td>0.85</td>
</tr>
<tr>
<td>S</td>
<td>0.32</td>
<td>0.45</td>
<td>0.18</td>
<td>0.85</td>
<td>0.85</td>
<td>1</td>
</tr>
</tbody>
</table>

Bold values indicate correlation coefficients >0.5 or < −0.5. Positive numbers indicate positive correlations; negative numbers indicate negative correlations.
The contributions of median-normalized score values for sample locations fall into two groups based on their highest contributing elements: Group 1, comprising select samples from Funeral Creek, sites proximal to three MVT showings (Zebra, Road and Samantha), and Group 2, which includes the rest of the sample locations (Fig. 6). Relative contributions of the metals of interest to each group are presented in Figure 7a and b, for stream silt sediments and filtered stream water, respectively. Group 1 always showed elevated contributions from Zn and Cd, whereas Group 2 had the highest contributions in Pb, although it also contributes about a quarter of the weight to Group 1. There are some sample sites that do not fit neatly into either group – these are manifested in the box plots (Fig. 7a and b) as outliers of Group 1 for Zn and Cd, but they tend to follow the rest of the trends for Group 1.

In the stream sediments, Se and Hg contribute much more to Group 2 than Group 1, with contributions of over 30 and 45 percent, respectively, making these trace metals comparable to the contribution by Pb.

In geological environments dominated by carbonate rocks, the geochemical signatures do not persist for a far distance downstream from interaction with mineralization and trends in dispersion are muted – hence an increased sample density is required to capture possible anomalies closer to mineralization. It is likely, however, that dilution plays a large role as well, as

Mineralogical Analysis

Mineral Identification

Synchrotron-based μXRD and μXRF showed that Zn and Pb were often found in trace amounts in goethite and hematite. Scatter plots of Zn counts v. Fe for individual μXRF maps showed good agreement (Fig. 8). In some cases, there were multiple Fe-Zn correlations, suggesting more than one population of Zn-hosting Fe minerals. Such trends were not observed for Pb. Goethite and hematite produced well-defined μXRD patterns (Fig. 9c), suggesting nanocrystallinity. Other minerals observed by synchrotron-based μXRD were ferrihydrite, lepidocrocite, chalcocypirte, cerussite, tennantite, arsentsumebite (Pb₂Cu(AsO₄)(SO₄)(OH)), montmorillonite, and nontronite. Montmorillonite and nontronite were often associated with secondary goethite and hematite. Detrital grains of sphalerite, galena, pyrite, dolomite, calcite, and quartz did not produce well-defined diffraction patterns from μXRD analysis, but were easily distinguishable based on EDS spectra collected from the SEM.

Dissolution, precipitation and alteration textures

Dissolution of Zn or Pb is the most commonly observed precipitated mineral in stream sediments (Fig. 9a and b). Evidence of cerussite precipitation has also been observed around the outside edges or within cracks and voids of quartz, dolomite, or clay grains and can occur as a smooth rim, needle-like fibres, botryoidal layers or cement.

Ocassional Fe oxyhydroxide grains have remnants of sulphide cores (Fig. 11). A weathered grain of detrital tennantite found in sediments from Rigor Mortis Creek contains an alteration rim enriched in Sb, As and Cu. Rare arsentsumebite (Pb₂Cu(AsO₄)(SO₄)(OH)) was identified from μXRD.

Discussion

In general, the results from this study are in agreement with the regional study of McCurdy et al. (2007). Absolute concentrations of the pathfinder elements do not appear anomalous when considered over the entire study area, particularly in the water samples. In geological environments dominated by carbonate rocks, the geochemical signatures do not persist for a far distance downstream from interaction with mineralization and trends in dispersion are muted – hence an increased sample density is required to capture possible anomalies closer to mineralization. It is likely, however, that dilution plays a large role as well, as
geochemical signals were often evident in the small tributaries to Prairie Creek, such as Rigor Mortis Creek, Harrison Creek, Funeral Creek, and other unnamed streams of a lower order (Fig. 4a–c), but geochemical signals in Prairie Creek were comparatively muted (Fig. 4d).

Metal concentrations in stream waters are magnitudes lower than the metal concentrations in the stream silt sediments, which are in turn magnitudes less than concentrations in the heavy mineral concentrates from the coarse fraction. The fact that anomalous concentrations of metals are greater in the stream silt sediments compared to the waters (Fig. 4a–c) supports the idea that the pathfinder elements are being weathered more physically than chemically (McCurdy et al. 2007), and that the slightly alkaline water conditions facilitate the attenuation of the trace metals onto the stream sediments. For exploration purposes, and in terms of absolute concentrations, it would be more efficient to investigate stream silt sediments or the heavy mineral concentrates than the water. However, if investigating heavy mineral concentrates, it would be important to remember that although the fraction upon which chemical analyses were performed on the heavy mineral concentrates is similar to that of the stream silt sediments (<0.25 v. <0.177 mm, respectively), this coarse-grained fraction of sediments had previously been subject to magnetic and heavy liquid separation, which would remove most of the gangue mineral grains that dilute the concentrations in the stream sediment samples.

Of the elements of interest in this study, Zn and Pb have the highest concentrations, often occurring magnitudes higher than the other elements of interest, in both the filtered water samples and the stream sediment samples (Fig. 4a–d). Zinc is usually found in higher concentrations than Pb, and shows a greater dispersion than Pb. This is likely due to high Zn/Pb in outcrops hosting sulphide mineralization near Rigor Mortis Creek and the Samantha showings, as supported by much higher Zn than Pb grades in drill core (Canadian Zinc Corporation 2012).

The elements of interest may be divided into groups based on correlations with each other. In the stream sediments, As + Cu + Sb (+Ag, ±Se) tend to be strongly correlated, as does Zn + Cd, and Hg + Ag (+Pb, ±Sb) (Table 1). In the heavy mineral concentrate (Table 2), similar groupings occur. Arsenic + Cu + Sb + Se were strongly correlated to each other as were Hg + Ag + Pb + Cd. Pairs of strong correlations were Sb + Ag, and Zn + Cd. These assemblages reflect the ore mineralogy of the quartz-carbonate-sulphide...
As, Cu, Ag and Sb are found together in tennantite-tetrahedrite; Zn and Cd are found together in sphalerite; and Pb and Ag are found in galena (Paradis, unpublished data).

Both Pb and Zn show only weak correlations with Fe and S, based on bulk sediment analysis (Tables 1 and 2). However, mineralogical analysis found that a large part of detectable Pb and Zn concentrations in the sediments occurred in association with Fe (oxy)hydroxides (both precipitated and as a result of Pb- and Zn-sulphide alteration, Figs 9a, b and 11) and non-altered detrital grains (both sulphides and oxides, Fig. 10). Although the bulk sediment analysis and the mineralogical analysis were performed on separate splits of the same sample, it would not be expected that any heterogeneity would be captured by the two different analyses such that the trends observed occur so consistently (i.e. that only grains where Pb and Zn were associated with Fe and S be present in the splits that were analyzed mineralogically, and only grains where Pb and Zn were not associated with Fe and S be present in the splits that underwent bulk sediment analysis). The discrepancy between these two methods of analysis (element correlations from bulk sediment analysis and element mapping by µ-XRF) may be due to the inherently subjective nature of the mineralogical analysis. When using the SEM to identify targets for synchrotron-based work, the researcher tends to choose grains that appear bright under back-scatter electron (BSE) mode (Jamieson et al. 2015). This has the effect of overlooking possible associations with minerals that are relatively dark under BSE mode. In the case of this study, the ‘bright’ grains under BSE mode were either detrital, or contained a high amount of Fe and were presumed to be Fe (oxy)hydroxides based on their lack of a sulphur signature. Thus, the only situations that elements of interest were identified in, were within detrital grains, or in association with iron (oxy)hydroxides. However, it is clear from
the correlation analyses that the elements of interest are not strongly correlated with either S or Fe, and so this leads to the conclusion that the grains analyzed under the SEM may not be fully representative of the entire sample.

Alkalinity and conductivity, although having wide ranges, tend to show broad trends and generally increase towards the bottom of the streams, as do Ca and Mg, indicating that their values are reflecting travel distance along a carbonate host lithology and other geomorphological elements, such as slope and catchment size of the stream (Fig. 4a–d). Lecomte et al. (2009) found that pH, conductivity, and major ions, were strongly related to catchment size and tended to increase downstream due to the increase in water-rock contact area, which increased interaction within the catchment. Lecomte et al. (2009) also concluded that low metal content in surface water was found to be related to slope influences, with relatively steeper areas showing less of a geochemical signal of trace metals due to a low residence time. In the Prairie Creek study area, the opposite seems to be true, as the three smaller streams have a steeper slope than Prairie Creek, but usually have a stronger geochemical signal of trace metals. In this study, the observation is more reflective of dilution rather than stream slope as Prairie Creek has a much higher flow than its tributaries.

The four streams sampled should not necessarily be compared to each other, as they differ in terms of the type of mineralization with which they possibly interact, as well as the degree of anthropogenic disturbance, and underlying lithology. Rigor Mortis Creek (Fig. 4a) was well suited to display interaction between stream media and vein mineralization, due to its nearly anthropogenically undisturbed nature. Increases in metal concentration from the initial values are likely due to vein mineralization, even though there is a lag between increasing concentrations and where the vein is projected to cross the stream (upstream of the first sampling point).

Although Funeral Creek is relatively anthropogenically undisturbed, the interpretation of the results is complicated by the fact that it encompasses two chemically different sources of trace elements – the MVT mineralization (Road Showing) near the head of the stream, and the quartz-carbonate-sulphide vein mineralization (Rico Showing) part way down the stream. The trace metal concentrations are distinctly different in the second half of Funeral Creek in comparison to the first half (Fig. 4b). Alkalinity increases by approximately 50 ppm,
conductivity increases by approximately 100 μS/cm, and ORP showed a large difference, decreasing by 200 mV to slightly reducing conditions. All metal concentrations show an increase after 2.4 km from the first sampling location, particularly in the stream sediments, which is suspected to be due to interaction with the vein mineralization. The sample site that was 2.4 km from the first sampling location also displayed orange-brown weathering of fractured calcareous shales (a change in bedrock from the previous sample point), which may indicate a higher iron sulphide content and consequently, more easily liberated metals.

The data collected from Harrison Creek (Fig. 4c) generally show a decreasing trend in metal content, both in sediments and waters, until 2.5 km from the first sampling location, when stream sediment concentrations increase, and at 3.0 km from the first sampling location, when water concentrations increase. The large increase at 2.5 km may be due to several factors. This sample point is located immediately downstream of visible exposures of the quartz-carbonate-sulphide vein, and so may be influenced by mineralization. It is also located adjacent to the waste rock pile and the elevated concentrations are also likely from leachate weathering waste rock, and possibly discharge from the mine portal at the top of the waste rock pile. The substrate in the area is mostly gravel, and a high hydraulic conductivity should be expected. A steel particle observed in a silt sample from this area confirms anthropogenic influence. Increase in water concentrations at 3.0 km from the first sampling location is likely due to treated mine water released directly into Harrison Creek immediately prior to the sample site.

The data collected from Prairie Creek (Fig. 4d) consistently show increasing concentration of trace metals in waters downstream of the mine, but decreasing concentrations in the stream sediments. The increase in metal concentrations in the water may be due to influence of the treated mine discharge from Harrison Creek, as the sample point 3 km from the first sampling location is at the confluence of Harrison Creek and Prairie Creek, and has elevated metal concentrations in water. However, there may also be an influence from Galena Creek, which is thought to interact with the vein mineralization and shows elevated concentrations of the pathfinder elements in the water (McCurdy et al. 2007). Otherwise, Prairie Creek does not show any great enrichment in pathfinder elements.

Median-normalized Score Values of Elements of Interest

When the summed score values were plotted according to their geographical location (Fig. 5), there were different chemical trends observed in the water samples when compared to the stream sediment samples, which may reflect the different mineralization styles in the area. Of the elements of interest, the signatures of Zn and Cd in water samples were more anomalous than stream sediment samples at sample locations where interaction between MVT mineralization is suspected to occur. The amount of secondary minerals suggest that there is a higher amount of dissolution and chemical weathering processes occurring within proximity of the MVT mineralization compared to the sample locations associated with vein style mineralization. MVT mineralization contains more marcasite (AMC Mining Consultants (Canada) Ltd. 2016), and occurs as growth within the vugs of sparry dolomite, in open spaces within breccias, or in fractures (Paradis 2007), which, due to an inherent increase in permeability, is more likely exposed to chemical weathering mechanisms, whether at an outcrop level or deeper within the bedrock. Conversely, there may be more rapid physical weathering and/or rapid attenuation of trace metals at the sample locations proximal to the quartz-carbonate-sulphide vein mineralization, such that the geochemical signal is partitioned into the sediment rather than water. This may be a reflection of the host rock, the nature of the mineralization, or the morphological properties of the valley within which the stream is found. Contrary to the MVT-style deposits, the vein mineralization is found as massive aggregates, to more disseminated and is also hosted in quartz, with minor calcite, and dolomite (Paradis 2007). Furthermore, the vein system has less pyrite than the MVT system. The decreased porosity and sulphide content of the vein mineralization (relative to the MVT mineralization) may result in less interaction of oxidizable minerals with possible weathering fluids and cause physical weathering to be the main mechanism by which the trace metals are mobilized.

Mineralogical Analysis

Results from the mineralogical analyses indicate that the chemical weathering is occurring on a scale that is smaller than the perceived stream geochemistry. A large portion of Zn and Pb, which is not
contained in ore-derived sulphides or carbonates, is associated with goethite, and sometimes hematite (Fig. 9). This association is often related to a near-total alteration of detrital sulphide grains (Fig. 11).

It is understood that Fe-(oxy)hydroxides have a strong influence on metal mobility and show high adsorption rates of metals with increasing pH, with adsorption edges for metals occurring between pH values of 4 and 7 (Cornell & Schwertmann 1996). The investigation of metals and their associations with one or several Fe-(oxy)hydroxides is not commonly analyzed on a micrometer scale, as was done in the analysis of stream sediment samples from the study area. Pixel counts of Zn and Fe within the micro-XRF element maps of weathered stream sediment grains showed multiple Fe-Zn corrections contained within Fe oxide particles (Fig. 8). The distinct trends are likely due to mixtures of goethite and hematite, as previous research has indicated that goethite can adsorb more Zn than hematite (McKenzie 1980; Stahl & James 1991; Pérez-López et al. 2011). Correlations between Pb and Fe do not display multiple populations.

In the stream sediment samples, goethite precipitation usually occurs on carbonate or quartz grain surfaces, while hematite occurs only in association with goethite and as a product of sulphide alteration, and is not found as a precipitate. The large variety of iron oxide/oxyhydroxide textures often made it difficult to differentiate between grains that have been altered, v. grains that have been precipitated; however, examples do exist that display obvious alteration textures, such as zonation, and obvious precipitation textures, such as fine, needle-like grains (Fig. 9).

Cerussite has been identified as a precipitate along the exposed edges and in the voids of quartz grains in silt sediments. In the stream sediment samples observed under the SEM, there is no evidence of smithsonite precipitation; however, detrital cerussite has been identified along the exposed edges and in the voids of quartz grains in silt sediments.
and smithsonite grains with dissolution textures were observed. The stability of these minerals is very sensitive to pH and alkalinity, and it seems likely that small changes in stream conditions lead to fluctuations in precipitation and dissolution of cerussite and dissolution of smithsonite. Detrital galena and sphalerite commonly display dissolution textures.

Conclusions

Lead and Zn appear to be the best candidates for use as pathfinder elements for these deposits, due to their high concentrations. Stream silt sediments and heavy mineral concentrates more readily show anomalous concentrations, because their absolute concentrations are much greater than the detection limits, in comparison to those measured in the water. However, when concentrations are normalized to their respective medians, influences from MVT mineralization are more evident in water than sediments, while the opposite is true of the quartz-carbonate-sulphide vein mineralization. Zinc appears to be more mobile than Pb, which is likely due to higher concentrations within the mineralization and lower solubility of Pb minerals. Higher concentrations of elements of interest do not seem to persist for great distances, and almost all evidence disappears due to dilution when tributaries enter in Prairie Creek. This is an important observation for exploration and remediation as stream size is clearly an important factor in the detection of geochemical anomalies.

Spearman correlation matrices indicate that the elements of interest are well-correlated with each other, but less correlated with major elements that may indicate associations with a host mineral. Zinc and Cd are most closely associated with Mg, which is likely a result of high Zn and Cd concentrations originating from the MVT mineralization, where sphalerite is found as a growth within vugs and voids of dolostone. There is no clear correlation between Pb or Zn, and Fe, which indicates that Fe-(oxy)hydroxides may not be as large of a control as indicated by the detailed mineralogical analysis.

Mineralogical analysis of the stream silt sediments show that apart from detrital material, trace metals, specifically Zn and Pb, are associated with goethite and hematite. These are found as alteration products of detrital material, such as rims on sulphides or as precipitated material closely associated with quartz, dolomite, or calcite. When the iron oxides are present as precipitates rather than alteration rims, they appear to be adsorbing the metals onto their exposed edges, as occasionally rims enriched in Pb and/or Zn. Zinc was found more often than Pb in association with iron oxide minerals. Mineralogical observations have shown evidence of precipitation and dissolution of metal-bearing phases, indicating active chemical weathering in the streams.
Fig. 11. Alteration of a sulphide grain replaced by goethite. (a) SEM photograph from a silt sediment sample taken near the Zebra showing. This grain was identified as goethite, possibly mixed with ferrihydrite. (b) Corresponding synchrotron XRF element map. Concentrations of all three elements mapped (Fe, Pb and S) increase towards the middle as the colouring becomes increasingly white. (c) EDS spectra of points on the grain. Red, blue, and green spectra correspond to red and blue stars on element map. The center of the grain is enriched in Pb and/or S, and is likely galena, while the surrounding iron-rich zones lack Pb and S but contain trace Zn. Please see online version for colour figure.

Acknowledgments and Funding

The authors wish to express their gratitude for the valuable input and assistance with microanalysis provided by Dr Anthony Lanzirotti. The authors would also like to thank Alan Taylor of Canadian Zinc Corporation for providing site access and much in kind support, as well as the entire crew at the Prairie Creek Mine for their assistance during the field work. This research was supported by the Targeted Geoscience Initiative 4 (TG4) program of the Geological Survey of Canada (GSC); NSERC; the Northwest Territories Geological Survey (NTGS); the Northern Scientific Training Program; and the Polar Continental Shelf Program. This research was supported by the Targeted Geoscience Initiative 4 (TG4) program of the Geological Survey of Canada (GSC); NSERC; the Northwest Territories Geological Survey (NTGS); the Northern Scientific Training Program; and the Polar Continental Shelf Program.

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