Geochemical and mineralogical controls on metal(loid) mobility in the oxide zone of the Prairie Creek Deposit, NWT

Drew Stavinga1,2, Heather Jamieson1*, Daniel Layton-Matthews1, Suzanne Paradis3 & Hendrik Falck4

1 Geological Sciences and Geological Engineering, Queen’s University, Kingston, ON, Canada
2 Present address: Arktis Solutions, Harrowsmith, ON, Canada
3 Geological Survey of Canada, Pacific Geoscience Centre, Sidney, BC, Canada
4 Northwest Territories Geological Survey, Government of Northwest Territories, Yellowknife, NT, Canada

*Correspondence: jamieson@queensu.ca

Abstract: Prairie Creek is an unmined high grade Zn-Pb-Ag deposit in the southern Mackenzie Mountains of the Northwest Territories, located in a 320 km2 enclave surrounded by the Nahanni National Park reserve. The upper portion of the quartz-carbonate sulphide vein mineralization has undergone extensive oxidation, forming high grade zones, rich in smithsonite (ZnCO3) and cerussite (PbCO3). This weathered zone represents a significant resource and a potential component of mine waste material. This study is focused on characterizing the geochemical and mineralogical controls on metal(loid) mobility under mine waste conditions, with particular attention to the metal carbonates as a potential source of trace elements to the environment.

Results include the identification of minor phases previously unknown at Prairie Creek, including cinnabar (HgS), acanthite (Ag2S), metal arsenates, and Pb-Sb-oxide. Anglesite (PbSO4) may also be present in greater proportions than recognized by previous work, composing up to 39 weight percent of some samples. Smithsonite is the major host for Zn but this mineral also contains elevated concentrations of Pb, Cd and Cu, while cerussite hosts Zn, Cu and Cd, with concentrations ranging from 6 ppm to upwards of 5.3 weight percent in the two minerals. Variable concentrations of As, Sb, Hg, Ag, and Se are also present in smithsonite and cerussite (listed in approximately decreasing order with concentrations ranging from <0.02 to 17 000 ppm). A significant proportion of the trace metal(loid)s may be hosted by other secondary minerals associated with mineralization. Processing will remove significant mineral hosts for these elements from the final tailings, although some may remain depending on whether the smithsonite fraction is left as tailings. Significant Hg and Ag could remain in tailings from cinnabar and acanthite that is trapped within smithsonite grains, which were found to act as a host for up to 53% of the Hg and 79% of the Ag contained in some samples.

In a mine waste setting, near-neutral pH will encourage retention of trace metal(loid)s in solids. Regardless, oxidation, dissolution and mobilization is expected to continue in the long term, which may be slowed by saturated conditions, or accelerated within smithsonite grains, which were found to act as a host for up to 53% of the Hg and 79% of the Ag contained in some samples.

The focus of this paper is on the deposit itself and the objective is to understand how Pb, Zn, Ag, Cu, As, Sb, Cd, Se, and Hg are mineralogically hosted in the oxide zone of the Prairie Creek deposit. Although the dominant minerals in this zone are carbonates rather than oxides, we have retained the term ‘oxide zone’ to encompass the presence of detrital galena, sphalerite, smithsonite and cerussite, and confirms active chemical weathering including the dissolution of primary Zn and Pb minerals, and precipitation of goethite and hematite that sequester Zn and Pb.

The trace elements listed above could be detected in many samples, Pb and especially Zn were typically orders of magnitude higher in concentration, and only these two are potential candidates as pathfinder elements (Skeries et al., in press). Mineralogical analysis of sediments proximal to Zn-Pb mineralization indicates the presence of detrital galena, sphalerite, smithsonite and cerussite, and confirms active chemical weathering including the dissolution of primary Zn and Pb minerals, and precipitation of goethite and hematite that sequester Zn and Pb.

The Prairie Creek Zn-Pb-Ag deposit is located 500 km west of Yellowknife in the southern Mackenzie Mountains and is completely surrounded by the recently-expanded Nahanni National Park Reserve (Fig. 1). The district contains several types of carbonate-hosted mineralization, including stratiform replacement sulphides, quartz-carbonate-sulphide veins, and classic Mississippi Valley-type (Paradis et al., 2007, 2015). The results of our research have implications for assessing the economic value of the oxide zone since understanding how potentially valuable trace elements such as Ag and Cu are...
hosted mineralogically will improve resource assessment, mineral processing and mine planning. Additionally, the results will help predict the geochemical controls on metal(loid) concentrations in drainage from future mine waste. Although widespread acid rock drainage is unlikely in this carbonate-rich environment, and Skerries et al. (in press) indicated limited mobility of trace elements on a regional scale, crushing metal-bearing waste rock and tailings can increase mineral reactivity and metal leaching even in pH-neutral drainage (e.g. Nordstrom 2011 and references therein). Moreover, there is limited information on how metals hosted in smithsonite and cerussite will behave in the mine waste environment, particularly if placed in water-saturated conditions.

The Prairie Creek mine site was developed in the 1980s but never reached production. The current owner, Canadian Zinc Corporation, intends to bring the property into production (Canadian Zinc Corporation 2010, 2014). Although acid rock drainage is not anticipated due to the substantial amount of carbonate associated with the mineralization, metal(loid) leaching occurs from the portal and is predicted from geochemical tests (MESH Environmental Inc. 2008). When mining commences, the tailings will be ground to a fine grain size (c. 80% at <80 µm), increasing their potential reactivity. Most of the Pb and Zn sulphides will be removed, and Pb and Zn oxides (cerussite and smithsonite) may be removed as well. Post-production plans include underground storage of all tailings as paste backfill. This may or may not include the smithsonite and cerussite fractions, depending on the final mine plan. Results from this research are used to predict the leaching behaviour of paste backfill made with the oxide zone tailings.

**Geology**

The Prairie Creek deposit is situated in an ancient paleo-basin comprised of Lower Palaeozoic deep water basinal rocks and platformal carbonates of the Mackenzie Shelf, consisting of limestones, dolostones, siltstones, shales and mudstones (Morrow & Cook 1987). The Prairie Creek rock (stratigraphic) sequence, from oldest to youngest, is comprised of the Sunblood Formation sandstone, Whittaker Formation dolostones, Road River Formation shales, and Cadillac Formation thinly bedded limy shales. In the northern part of the property, Arnica and Funeral Formation dolostones and limestones overlie this assemblage. Figure 2 illustrates the location of geologic units and structures relative to the Prairie Creek mine site and other Zn-Pb-Ag mineral occurrences.

Beginning in the Jurassic, the region surrounding the Prairie Creek deposit underwent three phases of deformation, resulting in doubly-plunging, faulted anticlines, broad, flat-bottomed synclines, steeply dipping reverse faults, and flatter thrust faults (Morrow & Cook 1987; Falck 2007). Fractures paralleling the north-trending reverse faults (e.g. Prairie Creek Fault) host vein-style mineralization, forming a corridor that extends for 16 km. The quartz-carbonate-sulphide veins occur predominantly within the argillaceous bioclastic shaly dolostone and overlying dolostones of the Upper Whittaker Formation and shales of the Road River Formation. The vein outcrops discontinuously along a north–south trending 16 km long corridor close to the axial plane of the north–south doubly-plunging anticline (Fig. 2). Where the vein system has been most extensively explored, the Main Quartz Vein (MQV) is associated with a north-striking, steeply east-dipping, near-vertical fault (Canadian Zinc Corporation 2010). The MQV width averages 2–3 m, and has a strike length of at least 2.1 km. Drill hole intercepts have demonstrated that the vein extends to at least 600 m below surface (Canadian Zinc Corporation 2010). The vein system is characterized by base metal mineralization, with the minerals of interest consisting of galena, sphalerite, pyrite, and tennantite-tetrahedrite as massive to disseminated sulphides in a quartz-carbonate-dolomite gangue matrix. Weathering and fluid flow along the fault has oxidized the upper portion of the vein, altering c. 15–20% of the total lead sulphides and 10% of the zinc sulphides into the Pb and Zn carbonate minerals cerussite (PbCO₃) and smithsonite (ZnCO₃) (Phase Geochemistry 2010). Although stratabound replacement and Mississippi Valley-type mineralization is also present on the property, they are not a significant component of the oxide zone resource of the Prairie Creek deposit. Consequently, they were not a focus of research and not discussed in detail in this paper.

**Results/Data Analysis**

**Field Sampling**

Fieldwork in August 2013 resulted in the collection of 29 samples of surface exposures of vein mineralization, 19 samples of the main quartz-carbonate-sulphide vein from the 930 level of the underground workings, 83 samples from drill-core (6 of which represented stratabound replacement sulphide mineralization), and 3 samples from the ore stockpile representing vein material of the...
870 underground level. Samples were chosen based on the presence of oxide zone mineralization and, where available, elevated concentrations of the elements of interest (Zn, Pb, Ag, Cu, As, Sb, Cd, Se, Hg). Seven additional samples of surface exposures were supplied by the Northwest Territories Geological Survey and 10 thin sections from the Geological Survey of Canada collection.
were analysed. Sample locations are shown in Figure 2 and included in the Supplementary Material.

Analytical methods and procedures

Lithogeochemistry

A subset of 53 samples, chosen to represent various degrees and styles of oxidation within the quartz-carbonate-sulphide veins, were digested via aqua regia and analysed for 45 elements by inductively coupled plasma - optical emission spectrometry (ICP-OES) at AGAT laboratories in Vancouver. A non-sulphide leach using ammonium acetate (for Pb) and ammonium chloride/ammonium acetate (for Zn) was used to obtain Pb and Zn concentrations that were considered to represent cerussite and smithsonite, although this was not explicitly tested. Samples with Ag concentrations greater than 500 ppm were subjected to Fire Assay Fusion with Gravimetric finish. Sample replicates, quartz blanks and internal reference materials were used for quality control and quality assurance. Replicate data on samples indicate an acceptable reproducibility (typically within 15%) for the 45 elements analyzed. Complete results, including results on blanks, replicates and reference materials are available in Stavinga (2014) and in the Supplementary Material.

Mineralogical and Trace Element Analysis

Polished thin sections were made from 38 samples selected on the basis of elevated concentrations of elements of interest, presence of Pb or Zn carbonates, and location within the deposit. These were examined by petrographic microscopy, and analysed by scanning electron microscopy (SEM) using a FEI MLA Quanta 650 with a field emission gun. SEM imaging was used for locating targets, and area-selective mapping was performed at a beam energy of 11 500 eV. X-ray diffraction (XRD) calibration (Walker et al. 2005, 2011) to monitor instrument drift and correct for elemental bias and laser yield. Raw data were plotted against the element-specific calibration curves created using GSC-1G (c. 2 – 10 ppm for most trace elements), GSD-1G (c. 30 – 70 ppm) and GSE-1G (c. 250 – 600 ppm) to quantify the ablated areas.

Synchrotron based trace element mapping using μXRF, and grain-scale micro-X-ray Diffraction (μXRD) were done at beamline X26A at the National Synchrotron Light Source. Micro XRF mapping was performed at a beam energy of 11 500 – 13 500 eV, with a beam spot size of c. 6 by 9 µm, a step (pixel) size of 3 – 25 µm, and a dwell time of 0.1 seconds/pixel. Micro XRD analyses were done at beam energy of 17 479 eV, using silver behenate and Al2O3 standards for μXRD calibration (Walker et al. 2005, 2011). Peak-matching software X-Pert HighScore (PANalytical) and a
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Table 1. Minerals identified by one or more microanalytical techniques within the quartz-carbonate-sulphide vein and stratabound sulphide-type mineralization

| Mineral          | Formula   |
|------------------|-----------|
| **Positively Identified Phases** |          |
| **Major Minerals** |          |
| Galena           | PbS       |
| Pyrite           | FeS₂      |
| Sphalerite       | (Zn,Fe)S  |
| Tennantite-      | (Cu₂Ag₂Fe₆Zn₃As₄S₁₃) - (Cu₂Fe₃Ag, |
| Tetrahedrite     | Zn₁₂₂SB₃S₁₃ |
| Anglesite        | PbSO₄     |
| Azurite          | Cu₅(CO₃)₂(OH)₂ |
| Calcite          | CaCO₃     |
| Cerussite        | PbCO₃     |
| Dolomite         | (Ca,Mg)(CO₃)₂ |
| Malachite        | Cu₂CO₃(OH)₂ |
| Smithsonite      | ZnCO₃     |
| Quartz           | SiO₂      |
| **Minor minerals** |          |
| Acanthite        | Ag₂S      |
| Bournonite       | Pb₃Cu₂S₈ |
| Cinnabar         | HgS       |
| Covellite        | CuS       |
| Goethite         | FeO(OH)   |
| Bindheimite      | Pb₃Sb₂O₄(O,OH) |
| Hydrozincite     | Zn₈(CO₃)₂(OH)₆ |
| Barite           | BaSO₄     |
| Christite        | Zn₈₂Cu₃₂(SO₄)₂(OH)₈·4H₂O |
| Adamite          | Zn₂₁(AsO₄)₄(0I) |
| Arsentumebite     | Pb₈Cu₂₃As₃O₇(SO₄)₂(OH) |
| Bayldonite       | Pb₈Cu₂₃Zn₃(AsO₄)₂(OH)₂ |
| Beaudantite      | PbFe₃⁺(AsO₄)₂(SO₄)₂(OH)₆ |
| Dufrite          | PbFeCu₃(AsO₄)₂(OH) |
| Mimette –        | Pb₈(AsO₄)₂Cl |
| Clinominette     | Pb₈Fe₃⁺(H₂AsO₄)₂(OH)₆ |
| Segnitite        | Pb₈Fe₃⁺(H₂AsO₄)₂(OH)₆ |

An additional 26 minerals were tentatively identified by SEM but not confirmed by µXRD (Stavinga, 2014).

recent mineral library were used to fit µXRD patterns to mineralogical phases. MicroXANES (X-ray absorption near-edge spectroscopy) of Sb-rich target spots was performed at sector 20 at the Advanced Photon Source to determine Sb oxidation state by comparison with standard materials Sb₂O₃, Sb₂O₄, and Sb₂O₅ using Athena© software (Ravel & Newville 2005).

SEM-based quantitative mineralogy using Mineral Liberation Analysis (MLA) was applied to eight thin sections that were representative of the oxidized mineralization. This method can allow for the identification of nearly all minerals in a thin section, based on a user-defined mineral reference library which, in this case, was developed from petrographic and SEM observations and µXRD. The relative proportions of the minerals and the distribution of particular elements amongst minerals can be calculated without bias. This was accomplished by combining the estimated average concentration of an element in a mineral with the relative mineral proportion in thin section as determined by MLA. Further details on analytical methods can be found in Stavinga (2014).

Overall, in the context of this study, analysis by EMP, with pre-selection of targets using SEM, proved to be most useful for determining the elemental composition of specific minerals. The small beam diameter of the EMP also allowed for precise targeting of fine textures, and avoidance of inclusions. Some phases, primarily the arsenates, proved too sensitive to analyze by EMP, since they would quickly be damaged and destroyed by any prolonged exposure under the beam. Detection limits from EMP are typically still in the hundreds of parts per million, with the lowest achieved being 113 ppm, limiting analysis of trace element concentrations. Analyzing for a large suite of elements is also impractical, as beam time on selected targets increases with each element selected for analyses, increasing damage to the site. Microanalysis using LA-ICP-MS proved essential in quantifying trace element concentrations, which were subsequently used to estimate the average concentration of elements within a particular mineral, and the distribution of elements. This method allowed for lower detection limits, approaching ppb level (with upper and lower bounds achieved ranging from 5000 ppm to 20 ppb), as well as the ability to analyze for a larger list of elements compared to EMP. The laser ablation line could also allow for the detection of changes in element composition across a mineral crystal or structure. A larger beam diameter allowed for a greater area to be analyzed for more representative results. However, the larger sample volume analysed made it difficult to avoid inclusions of separate phases within the mineral of interest and precluded analysis of finer targets, while greater penetration depth means that any shallow, underlying phases may also be ablated and influence results. The comparative merits of EMP and LA-ICP-MS observed during this study are generally well understood and were consistent with those observed by others (Gauert et al. 2010). MLA proved to be the best tool for estimating relative proportions of minerals and specific element speciation, a term which in this case can be used to describe the solid phase that hosts the element (Ure 1991; Templeton et al. 2000). Synchrotron-based microanalysis was critical in identifying unknown phases via microXRD, and providing important insight into the distribution of elements of concern and their valence states that would not otherwise have been known (i.e. Hg and Se associations, and Sb oxidation state). Each analytical technique complemented the others, and their combined use greatly increased the quality of the results achieved. A comprehensive understanding of how elements are mineralogically hosted would not have been achieved with any single method.

### Results

#### Lithogeochemistry

In general, most samples of the oxidized MQV show higher than average concentrations of Ag (422 ppm), As (1587 ppm), Cu (8786 ppm), Cd (1374 ppm), Hg (491 ppm), Pb (16.4%), and Sb (3563 ppm) when compared to the adjacent carbonate host rock (Fig. 3). Except for two samples, Se was mostly below detection limit (<50 ppm). Total Zn concentrations are relatively consistent between the vein (15.8%) and the immediately adjacent host rock of the hanging wall (15.2% for a sample within 10 cm of the vein), but are lower in the footwall. Non-sulphide Zn concentrations follow a similar pattern, with an average concentration of 9.9 and 8.2% in the vein and hanging wall rocks, respectively. Iron concentrations were similar between the carbonate footwall (0.4%), hanging wall (0.4%), and vein material (0.6%). Although Cd and Hg have higher average concentrations in the vein than the host rocks, their values generally fall within the range of concentrations occurring within the hanging wall rocks, with the exception of a few outliers. Digestion by non-sulphide leach found non-sulphide Pb concentrations are generally higher (average 8.1%) in the mineralized vein, are slightly lower in the hanging wall rocks (average 3.6%), and much lower in the footwall rocks (average 0.3%). The complete analytical results and correlation matrices for the lithogeochemical analyses can be found in Stavinga (2014).

#### Mineralogy

Table 1 lists all minerals identified through a combination of analytical techniques, including SEM, EMP, XRD and synchrotron-
based μXRF and μXRD. The most common and abundant minerals identified consist of the primary sulphides (galena, sphalerite, pyrite) and sulfosalts (tetrahedrite-tennantite), the host rock and gangue minerals (calcite, dolomite, quartz), and the secondary metal carbonates (smithsonite, cerussite, malachite, azurite). Additional secondary oxidation products that were identified include anglesite, arsenates, covellite, bindheimite, acanthite, cinnabar, and goethite. Tentatively identified phases (such as tenorite and olivenite), 26 in all, were distinguished by SEM, but did not differflact well enough to be firmly identified by μXRD.

**Major and Trace Element Geochemistry**

Analyses of the metal carbonates and anglesite by EMP and LA-ICP-MS indicate that they host many of the elements of concern, including Ag, Cu, As, Hg, Sb, Cd, and Se. Elemental concentrations presented in Figure 4 suggests some elements are preferentially hosted by certain minerals over others; for instance Ag and Se are higher in cerussite and anglesite, while Cd is more concentrated in smithsonite. Anglesite also contains higher concentrations of Ag, As, Cu, Pb and Se than the Pb and Zn carbonates. Based on EMP and LA-ICP-MS analyses, smithsonite, in addition to being a major host for Zn, is also a host for Cu (384 – 22 000 ppm), Cd (301 – 14 000 ppm), Sb (28 – 17 000 ppm), Hg (593 – 5679 ppm), As (10 – 2650 ppm), Pb (1 – 1021 ppm) and Se (<0.02 – 29 ppm) in approximately decreasing order. Cerussite, the major secondary host for Pb, also contains Zn (96 – 53 000 ppm), Cu (8 – 24 000 ppm), Sb (1 to >5000 ppm), Ag (0.2 to >2000 ppm), Hg (<675 – 8139 ppm), Cd (6 to >1600 ppm), As (0.3 – 3558 ppm) and Se (0.02 – 30 ppm) in order of decreasing concentration, whereas anglesite is host to Pb, Cu, Zn, Sb, Hg, Ag, Cd, As, Se and Sb (see Table 2 for concentrations). Malachite and azurite were also found to attenuate Cu, Zn, Pb, As, and Sb in decreasing order. Qualitative SEM and μXRF analyses further indicated malachite/azurite as possible hosts for Cd, Ag and Hg as well. The geochemistry discussed above agrees well with the commonly observed trace elements found in smithsonite and cerussite in other deposits (Boni & Large 2003; Katerinopoulos et al. 2005; Balassone et al. 2008; Garcia-Guinea et al. 2009; Lin et al. 2010).

Previous work (MESH Environmental Inc. 2008; pHase Geochemistry 2010) attributes dissolution of the metal carbonates as the primary source of mobilized metal(loid)s from simulated tailings material. However, our results indicate that some of the metal(loid)s are actually hosted in minerals other than smithsonite and cerussite. A combination of element mapping and μXRD was used to identify additional secondary minerals where diffraction patterns were clear. In many cases, elements of interest are hosted by secondary minerals present as small inclusions within smithsonite and cerussite, as illustrated in Figures 5 and 6. Mercury is hosted by cinnabar (Figs 5a and 6a), and Ag is hosted by acanthite (Fig. 6b). Arsenic is hosted by several arsenate minerals (see Table 1; Fig. 6b, c and d), which also attenuate concentrations of Pb, Cu and Zn in decreasing order of significance (assuming equal proportions of each positively identified phase). Most of the Sb is hosted in bindheimite, a Sb(V) bearing member of the stibiconite group of the pyrochlore supergroup (Fig. 5b). MicroXANES analysis of Sb-rich hotspots identified as bindheimite indicated a mixture of Sb(III) and Sb(V) (Fig. 7), suggesting substitution of Pb by Sb(III).

Trace element mapping employing synchrotron-based μXRF revealed the arsenates to be a potentially significant host of Hg and Se as well. SEM and μXRF also found bindheimite to host Cd, Zn, As, Cu and possibly Ag and Hg. Cinnabar was found to contain Se, whereas acanthite hosts Hg and Zn and covellite was found to hold Cu, Pb, Ag and Zn. Goethite, which replaces pyrite and is also a common inclusion in smithsonite, contains detectable concentrations of metal(loid)s under qualitative SEM and μXRF analysis, primarily Pb, Sb, Zn, As, and Cu (Fig. 6e), and possibly Hg and Se as well. The metal(loid)s are concentrated along the edges of goethite grains or evenly dispersed throughout them. Lead is the dominant metal of interest hosted by goethite, in both pyrite replacement rims and smithsonite inclusions. Mineral mapping by μXRF also illustrates the textural relationship of minerals hosting the elements of interest. For example, Figure 6c and d shows arsenate minerals forming rims along the edges of other minerals.

![Fig. 4. EMP and LA-ICP-MS results for selected elements of interest in secondary oxide minerals. EMP concentrations below detection limit and LA-ICP-MS concentrations greater than one order of magnitude above the calibration curve limit are omitted.](http://geea.lyellcollection.org/)
Table 2. Concentration ranges from EMP and LA-ICP-MS analysis of primary sulphides and sulfosalts and secondary oxide minerals

| Mineral                  | Method     | Ag  | As   | Ca   | Cd   | Cu   | Fe   | Hg   | Mg   | Mn   | Pb   | Sb   | Se   | Zn   |
|--------------------------|------------|-----|------|------|------|------|------|------|------|------|------|------|------|------|
| Galena                   | EMP        | –   | <290 | –    | –    | <290 | –    | –    | –    | –    | –    | <290 | –    | <433 |
|                          | LA-ICP-MS  | 25  | 2 to >2000 | 4  | 4 to 384 | 3  | to >2000 | 4  | 4 to 384 | 3  | to >2000 | 6  | 6 to >5000 | 2  | to >5000 |
| Average                  |            | 915 | 34   | –    | 96   | 713  | 236  | –    | –    | –    | 86.5 | 537  | 6    | 1011 |
| Sphalerite               | EMP        | <324| <659 | –    | <936 | <5516| <262 | <262 | <497 | <262 | <1972 | <1972 | <1294| <1294|
|                          | LA-ICP-MS  | 36  | 2 to >2000 | 2  | 2 to >2000 | 2  | 2 to >2000 | 3  | 3 to >2000 | 7  | 7 to >2000 | 12 | 12 to >2000 | 20 | 20 to >5000 |
| Average                  |            | 36  | 36   | –    | 36   | 36   | 36   | –    | –    | –    | 36   | 36   | 36   | 36   |
| Tennantite-Tetrahedrite  | EMP        | <323| 1 to 5    | 1.5 | 1 to 5  | 1.5 | 1 to 5 | 1.5 | 1 to 5 | 1.5 | 1 to 5 | 1.5 | 1 to 5 | 1.5 | 1 to 5 |
|                          | LA-ICP-MS  | 36  | 36   | –    | 36   | 36   | 36   | –    | –    | –    | 36   | 36   | 36   | 36   |
| Average                  |            | 36  | 36   | –    | 36   | 36   | 36   | –    | –    | –    | 36   | 36   | 36   | 36   |
| Pyrite                   | EMP        | <323| <445 | –    | <2020| <507 | 616  | <491 | <491 | <491 | <491 | <491 | <491 | <491 |
|                          | LA-ICP-MS  | 36  | 36   | –    | 36   | 36   | 36   | –    | –    | –    | 36   | 36   | 36   | 36   |
| Average                  |            | 36  | 36   | –    | 36   | 36   | 36   | –    | –    | –    | 36   | 36   | 36   | 36   |
| Bournonite               | EMP        | <323| <445 | –    | <2020| <507 | 616  | <491 | <491 | <491 | <491 | <491 | <491 | <491 |
|                          | LA-ICP-MS  | 36  | 36   | –    | 36   | 36   | 36   | –    | –    | –    | 36   | 36   | 36   | 36   |
| Average                  |            | 36  | 36   | –    | 36   | 36   | 36   | –    | –    | –    | 36   | 36   | 36   | 36   |
| Smithsonite              | EMP        | <385| 1 to 10 | 10 | 10 to >2600 | 1  | 10 to >2600 | 1  | 10 to >2600 | 1  | 10 to >2600 | 1  | 10 to >2600 | 1  | 10 to >2600 |
|                          | LA-ICP-MS  | 1   | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    |
| Average                  |            | 1   | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    |
| Cerussite                | EMP        | <578| <4350 | <435 | <4350 | <435 | <435 | <435 | <435 | <435 | <435 | <435 | <435 | <435 |
|                          | LA-ICP-MS  | 0.2 | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  |
| Average                  |            | 0.2 | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  | 0.2  |
| Anglesite                | EMP        | <578| <578 | <578 | <578 | <578 | <578 | <578 | <578 | <578 | <578 | <578 | <578 | <578 |
|                          | LA-ICP-MS  | 1320| 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 |
| Average                  |            | 1320| 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 | 1320 |
| Malachite                | EMP        | <385| 973  | 2047 | 973  | 2047 | 973  | 2047 | 973  | 2047 | 973  | 2047 | 973  | 2047 |
|                          | LA-ICP-MS  | 172 | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  |
| Average                  |            | 172 | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  |
| Malachite/Azurite        | EMP        | –   | 1653 | –    | –    | 1653 | –    | –    | 1653 | –    | –    | 1653 | –    | 1653 |
|                          | LA-ICP-MS  | 172 | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  |
| Average                  |            | 172 | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  | 172  |

Values below detection limit are listed as ‘<[Detection Limit]’. Values one order of magnitude above or below the ICP-MS calibration curve limit are listed as ‘>[Limit]’ and ‘<[Limit]’, respectively. No Hg standard was available for LA-ICP-MS. Average concentrations were calculated using either half the value of the detection limit, the Maximum Likelihood Estimator Method or Kaplan–Meir Method (as described by Helsel 2005, 2012) depending on the number of non-detects.
Both Cd (Fig. 6f) and Cu (not shown) are concentrated within discrete bands in smithsonite.

Mineral mapping of thin sections by SEM-MLA provides information on mineral proportions, grain sizes and mineral associations (Fig. 8). These results reveal that anglesite is present in greater proportions than previously thought (e.g. MESH Environmental Inc. 2008), with some samples composed of up to 39 wt% anglesite v. 11 wt% cerussite. The other secondary phases identified may also exist in high enough proportions to influence metal(loid) mobility. The grain sizes of some minerals, particularly cinnabar and acanthite, were relatively fine and found primarily as inclusions in smithsonite (Fig. 8C). Textural evidence of dissolution of the metal carbonates and other secondary phases is also seen in strongly weathered material.

Fig. 5. Backscattered-electron images and energy-dispersive spectra showing elements of interest hosted in mineral inclusions included in smithsonite (a) Hg-S phase; (b) Pb-Sb-O phase. Mineral composition based on µXRD.

Fig. 6. Element maps collected by synchrotron-based µXRF showing: (a) cinnabar inclusions in smithsonite; (b) acanthite with a rim of secondary arsenate; (c) arsenate inclusions in smithsonite with trace amounts of Hg and Se; (d) malachite with a rim of secondary arsenate; (e) pyrite altering to goethite with trace amounts of As and Pb; (f) Cd concentrated in smithsonite banding. Mineral composition based on µXRD. Note that the colours correspond to detector counts and vary from element to element.
Discussion

Trace Element Geochemistry and Speciation of the Oxide Zone

The distribution of elements amongst minerals in each thin section analyzed by MLA is estimated by combining the estimated average concentrations for each mineral (Table 2) with the modal mineralogy calculated by the MLA software (details in Stavinga 2014). Thus, the major sources of elements of interest are revealed for each sample (Fig. 9). Reconciliation assays that compare the total concentration of each element calculated by MLA for a thin section agree fairly well with the overall whole rock geochemical results, typically falling within the range of measured total element concentrations. The heterogeneous nature of the mineralization, however, means a direct comparison of concentrations between the same samples is less reliable, resulting in differences of up to 19 weight percent as the material used for each analysis can vary in mineral proportions. Nevertheless, this suggests that speciation analysis of a large suite of thin sections could give concentrations similar to lithogeochemical analysis of whole rock samples, and could therefore be relatively representative of the overall geochemistry of the quartz-carbonate sulphide vein.

The MLA speciation assessment found that out of eight thin sections analyzed, the following minerals acted as the primary host (among the secondary phases) for an element of interest:

1. Ag – cerussite (57%), anglesite (21%), acanthite (79%), smithsonite (66%)
2. As – arsenate (95%), smithsonite (96%)
3. Cd – anglesite (7%), smithsonite (99%)

Fig. 7. K-edge energy spectra from synchrotron-based μXANES of Sb targets. Bindheimite and smithsonite-cinnabar targets lie between the Sb(III) and Sb(V) K-edge, suggesting a mixed valence. Adamite matches with the Sb(V) K-edge, suggesting it hosts primarily Sb(V).

Fig. 8. Examples of mineral maps generated by SEM-MLA used for calculating mineral proportions and observing grain size and textures. (a) Strongly oxidized sample of quartz-carbonate-sulphide vein from the underground mine containing abundant anglesite (yellow); (b) Strongly oxidized sample of quartz-carbonate-sulphide vein from surface, containing abundant arsenate (purple) and bindheimite (yellow-green); (c) Cinnabar and associated arsenate and bindheimite inclusions in smithsonite. White areas represent holes in the thin section.
The maximum percentage of the element found to be hosted by the mineral is also listed above. Thus, in addition to the metal carbonates smithsonite and cerussite, a wide array of other secondary oxidation products are a major source of elements of concern in material from the oxide zone. It is important to understand the concentrations of elements hosted by these secondary minerals, as the release of potentially hazardous metal(loid)s will depend upon their stability in a mine waste setting.

**Sulphide Oxidation under Alkaline Conditions**

Oxidation of the sulphides is occurring at Prairie Creek although this does not result in acid conditions due to the alkalinity and effective buffering capacity offered by the carbonate host rocks. While sphalerite oxidation decreases with increasing pH, it begins to increase again above pH 7, primarily due to the influence of the oxidant O2 (Ziping et al. 2012). Oxidation may also be aided in part by armouring of calcite grains by gypsum and hydrous ferric oxide, inhibiting fast neutralization of the acidic solution produced by oxidation of the sulphides and allowing the establishment and stability of an acidic pH within the oxidation zone (Reichert & Borg 2008). At Prairie Creek, dissolution and alteration of sphalerite is more apparent than galena, likely due to anglesite and cerussite rims protecting the galena from further oxidation (Stavinga 2014). This may explain why in highly oxidized samples, the only trace of original sulphides is typically galena, as is common in many oxidized sulphide ores as well as in many gossans (Reichert & Borg 2008; e.g. Jeong & Lee 2003). Sulphide oxidation releases major and trace elements to pore water, and under alkaline conditions the aqueous concentration of some elements (i.e. Zn, Pb) will be limited by the solubility of secondary minerals hosting major concentrations of these elements such as smithsonite (Zn) and cerussite (Pb). Other elements will be limited by their inclusion as trace constituents in major secondary minerals, like As in smithsonite and Se in cerussite, or as major constituents of minor secondary minerals, such as Sb in bindheimite and Hg in cinnabar. Dissolution of these secondary minerals could result in the release of potentially hazardous concentrations of major and trace elements in the environment.

**Prediction of Metal(loid) Mobility from Mine Waste**

Samples analysed in this study were collected from quartz-carbonate-sulphide veins in situ, except samples collected from drill core (including stratabound replacement massive sulphides), which have been stored at surface for up to 22 years, and the 870 underground level, which have been undergoing weathering in the ore stockpile for c. 30 years. Little mineralogical difference was observed between the samples collected directly from the orebody and surface showings and those from stored drill core and the stockpile. Upon the commencement of mining, most Pb and Zn sulphides will be removed, and the finely ground tailings will be mixed with binders and cement to form a paste backfill for potential storage underground. This may or may not include the smithsonite and cerussite fractions, depending on the final mine plan. Previous studies (MESH Environmental Inc. 2008) have suggested that the metal carbonates will dissolve and contribute to the alkalinity and metal(loid) content of the mine water, with smithsonite having a greater potential to dissolve than cerussite. This is due to the tendency of cerussite to alter to anglesite rather than dissolve and release Pb ions (Sato 1992); the release of Zn ions from smithsonite should therefore occur at a greater rate. With the exception of strongly weathered surface showings, samples usually show only minor dissolution of the metal carbonates under the current in situ conditions. However, should dissolution of the metal carbonates occur, Zn, Pb and other trace elements of concern would be released into the pore waters, increasing concentrations significantly if conditions do not favour their attenuation. The dissolution of metal carbonates, in addition to the oxidation of sulphides, is therefore anticipated to be a major factor controlling the mobility of the trace elements. Although typically present in minor abundance relative to the metal carbonates, with the possible exception of anglesite, results of the speciation analysis suggest that dissolution of the secondary phases will be a prevailing factor on metal(loid) mobility.

The response to infiltration of the tailings by mine water can be anticipated to be similar to the reactions in the ore stockpile with rainwater infiltration. The mineralogical characterization by Skerries (2013) of sediments present in the stockpile, which has been exposed for 30 years, identified dissolution textures present in the sulphides, metal carbonates (smithsonite, cerussite) and anglesite. However, the formation of secondary rims on sulphides, such as cerussite and anglesite on galena and goethite on pyrite, should slow their dissolution and release of metal(loid)s. Goethite is the most common Fe-(oxy)hydroxide formed under alkaline conditions.
change in conditions, but whether concentrations will be low dissolution of the secondary oxidation products. Metals are likely sulphide oxidation, but reducing conditions could increase continue to limit dissolution as well as encourage precipitation and release rates relatively low under the present oxidizing, alkaline covellite, and Se from a combination of anglesite, cinnabar and acanthite that is trapped within smithsonite grains. Hosted by the other secondary minerals, including azurite/malachite, metal(loid)s; however, smithsonite, and possibly anglesite may oxidation products on trace element mobility in the oxide zone of geochemical behaviour under water-saturated conditions is uncertain (Stavinga 2014).

Conclusion
There is generally good agreement between the results of this study and previous geochemical characterization studies (MESH Environmental Inc. 2008; pHase Geochemistry 2010); however the influence of previously unknown and/or unreported secondary oxidation products on trace element mobility in the oxide zone of the Prairie Creek deposit may be greater than has been indicated. Processing from ore to tailings will remove significant sources for the metal(loid)s; however, smithsonite, and possibly arsenite may subsequently remain as the major source for many of them (particularly Zn, Cd and Pb), with smaller to greater proportions hosted by the other secondary minerals, including azurite/malachite, the arsenite, bindheimite, cinnabar, acanthite and goethite. These include significant Hg (an environmental concern) and Ag (a valuable commodity) components that could potentially be in the form of cinnabar and acanthite that is trapped within smithsonite grains. Mobilized As may be released primarily from arsenites, with Sb coming from bindheimite, Cu from anglesite, malachite, azurite and covellite, and Se from a combination of anglesite, cinnabar and arsenates.

Overall, the metals released by sulphides and sulfosalt are largely controlled by the secondary oxidation products, which keep release rates relatively low under the present oxidizing, alkaline conditions. The expected near neutral to alkaline pH conditions that will occur in a mine waste setting, including paste backfill, should continue to limit dissolution as well as encourage precipitation and attenuation of the metals of concern. The stability of many of the secondary phases is highly sensitive to pH however, and a change to even slightly acidic conditions may greatly increase their dissolution along with the sulphides. Saturation of the tailings will greatly slow sulphide oxidation, but reducing conditions could increase dissolution of the secondary oxidation products. Metals are likely to re-precipitate or be attenuated by more stable phases with each change in conditions, but whether concentrations will be low enough to meet water quality guidelines is uncertain.

Acknowledgements and Funding
The authors would like to thank the Geological Survey of Canada, particularly the TGI-4 program for supporting this research. Canadian Zinc Corporation provided access, in-kind support and advice. Funding was also provided by the Northern Studies Training Program, the Society of Economic Geologists, and an NSERC Discovery Grant to H.E. Jamieson. Synchrotron analysis was done at beamline X26A, National Synchrotron Light Source, Upton, New York. Shannon Shaw of pHase Geochemistry was particularly helpful.

Correction notice: The original version was incorrect. This was due to an error in the author list: D. Layton-Matthews has now been included.

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APPENDIX 1

Supplementary Field Sampling Methods

Nineteen grab samples were collected from exposures of the main quartz-carbonate-sulphide vein in the underground 930 level adit. Because the 870 level adit was not accessible in 2013, samples of mineralized vein material originating from the 870 level were collected from the historic ore stockpile on the mine site, resulting in a total of 22 samples from the underground workings. Sample locations from the underground adits are shown in Figure A1 (provided in the Supplementary material). Thirty-eight drill holes were sampled in order to provide a suite of 83 samples spatially distributed across the deposit and representative of the types of mineralization and various degrees of oxidation and alteration. A summary of the surface, adit and core samples selected for subsequent analysis by one or more of the analytical methods described in this paper are included in Table A1 (provided in the Supplementary material).

Supplementary Lithogeochemistry Methods

Forty-three whole rock samples were analyzed for 45 elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, In, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, U, V, W, Y, Zn, Zr). Five separate samples were used for replicate testing. Replicate and reference material results are included in Table A2 (provided in the Supplementary material). Elements typically had an acceptable relative percent difference (RPD) between originals and replicates of within 15%.

Supplementary Electron Microprobe Methods

A total of 17 thin section samples were analyzed for 13 elements (Ag, As, Ca, Cd, Cu, Fe, Hg, Mg, Mn, Pb, Sb, Se, Zn) in 9 phases (excluding unknowns; smithsonite, cerussite, malachite, anglesite, sphalerite, pyrite, galena, tennantite-tetrahedrite, bournonite). LIF, PET and TAP diffraction crystals detected element wavelengths for each mineral phase. Large area and high intensity LIF and PET crystals are indicated with an L and H, respectively. Measured X-rays using the LIF crystal included: Zn Kα (smt). Measured X-rays using the LIF crystal included: Fe Kα (smt, mcl, cer, ang, sp, gn, ttr, py, bnt); Mn Kα (smt, cer, ang); Cu Kα (smt, mcl, cer, ang, sp, gn, ttr, py, bnt); Zn Kα (smt, mcl, cer, ang, gp, ttr, py, bnt). Measured X-rays using the PET crystal included: Sb Lα (smt, mcl, cer, ang, sp, gn, ttr, py, bnt); Pb Mα (cer, ang, smt, mcl, sp, gn, ttr, py, bnt); S Kα (sp, gn, ttr, py, bnt). Measured X-rays using the PETH crystal included: Pb Mα (smt, cer, ang); Ca Kα (smt, cer, ang); Cd Lα (smt, mcl, cer, ang, sp, gn, ttr, py, bnt); Sb Lα (smt, cer, ang); Ag Lα (smt, mcl, cer, ang, sp, gn, ttr, py, bnt); Hg Mα (smt, mcl, cer, ang, sp, gn, ttr, py, bnt); Se Lα (smt, mcl, cer, ang). Secondary ‘working’ standards of sphalerite and tetrahedrite and a primary galena standard were analyzed as unknowns to test the instrument calibration for analysis of sulphides and sulfosalts. Due to a lack of working standards, the calibration could not be tested for the metal carbonates. The data were processed using the CITZAF V3.5 online software program for JEOLO™ written by J. T. Armstrong (California Institute of Technology).

The lower limit of detection (LLD) was calculated using the formula below for each spot analyzed by electron microprobe. Abbreviations are as follows: ZAF, total matrix correction factor; std, standard; unk, unknown; bkg, background; C, concentration (wt %); I, intensity ((s*nA)−1); t, count time (s); curr, current (nA) (pers. comm. B. Joy, 2013).

\[
\text{LLD (3\sigma)} = 3\times ZAF \times \frac{C_{\text{std}}}{I_{\text{std,net}}} \times \sqrt{2} \times \sqrt{\frac{I_{\text{unk,bkg}}}{I_{\text{unk,bkg}} \times \text{curr unk}}}
\]

\[
\text{LLD (2\sigma)} = 2 \times ZAF \times \frac{C_{\text{std}}}{I_{\text{std,net}}} \times \frac{I_{\text{unk,bkg}}}{I_{\text{unk,bkg}} \times \text{curr unk}}
\]

Supplementary Laser Ablation ICP-MS Methods

Of the 9 elements of interest detected in this study (Zn, Pb, Ag, As, Cd, Cu, Hg, Sb and Se), Hg was not considered due to a lack of standard data. Published and preferred data for the standards used (GSC-1G, GSD-1G, GSE-1G and BHVO-2G) were found on the Geological and Environmental Reference Materials database (http://georem.mpch-mainz.gwdg.de/sample_query_pref.asp) and are included in the Supplementary material Table A3. A total of 40 analyses were conducted on 5 phases (smithsonite, cerussite, anglesite, azurite, galena). Analyses were conducted using the line technique for laser ablation of in-situ minerals. Data were compiled and interpreted using Thermo Fisher Scientific PlasmaLab™ software. Concentrations one order of magnitude above or below the upper and lower limit of the calibration curve were considered unreliable and thus, not used (pers. comm., D. Layton-Matthews, 2014).

Supplementary Mineral Liberation Analyzer Methods

Eight thin sections were analyzed using Mineral Liberation Analyzer Automated Mineralogy Software at Queen’s University. The software used the back-scatter electron imagery and energy dispersive X-ray analysis of an SEM to analyze each particle’s shape, size, and mineralogical information. The EDS data are then compared to a user-generated Mineral Reference Library consisting of known phases and corresponding EDS spectra to classify each particle (Buckwalter-Davis 2013, and references therein).

The percentage of a particular element within a thin section that is hosted by a specific mineral phase was calculated by combining the estimated average concentrations for each mineral with the modal
mineralogy calculated by MLA software. Average concentrations for elements of interest are estimated using a variety of methods. The mean was simply used when an analysis gave all detected values. When an analysis gave a mix of detected values and non-detects, the maximum likelihood estimator (MLE) method was used, as described by Helsel (2005, 2012). If the sample size was small (typically <25) and/or an adequate distribution of the data (e.g. Normal, Lognormal, etc.) was unable to be determined, the nonparametric Kaplan-Meier method was used to estimate the mean (Helsel 2005, 2012). If less than three detected values and two separate detection limits were available, preventing reliable use of the Kaplan–Meier method, then simple substitution using half the value of the detection limit in place of non-detects was used. Elements which had no detected values in certain minerals were not given an estimated average. Computations were completed using Minitab® software.