

Sulphides and nonsulphides of the Prairie Creek district; update on the isotope geochemistry

S. Paradis

*Geological Survey of Canada, 9860 West Saanich Road, Sidney, BC, V8L 4B2
suzanne.paradis@NRCan-RNCan.gc.ca*

Abstract

The Prairie Creek Zn-Pb-Ag district comprises three distinct types of carbonate-hosted sulphide mineralization that includes quartz-carbonate-sulphide veins, stratabound replacement sulphides, and classic Mississippi Valley-type. The surface portion of the veins (down to a depth of 200m at the mine site) has undergone extensive oxidation, forming zones rich in smithsonite, cerussite, azurite, malachite, anglesite and hydrozincite. The pyrite and sphalerite within the Mississippi Valley-type showings are oxidized to hematite/goethite and smithsonite, respectively. The stratabound replacement sulphide lenses, which do not outcrop, are not pervasively oxidized.

Here we report results of a stable isotope study of carbonates from all three types of mineralization and associated oxidation zones. The results indicate that oxidation occurred under supergene conditions from local meteoric waters that interacted with the host carbonates at low temperatures. The oxidation of sulphides and formation of nonsulphide Pb, Zn, Cu minerals postdates the Laramide orogeny and is continuing at the present time.

Introduction

The Prairie Creek Zn-Pb-Ag district in Northwest Territories (NT), Canada, is located in shales and carbonates of the Prairie Creek Embayment, a north-south (N-S) paleo-depression of the Selwyn Basin filled by Ordovician to Devonian platformal and basinal sediments (Figure 1). It hosts three distinct types of carbonate-hosted Zn-Pb-Ag sulphide mineralization: a) quartz-carbonate-sulphide veins, b) stratabound replacement sulphides (SRS), and c) classic Mississippi Valley-type (MVT) deposits (Fraser, 1996; Findlay, 2000; Paradis, 2007; AMC Mining Consultants, 2014). The surface and near-surface exposures of the vein and MVT occurrences have been extensively oxidized.

Herein we present a brief overview of the regional and mine geology, and focus on the mineralogy and isotope geochemistry (C, O, Sr) of the metal carbonates (referred to as nonsulphides in this paper) and their carbonate host rocks. The objectives of this paper are to 1) introduce the deposits for the benefit of companion papers of Stavinga et al. (2015), and Taylor et al. (2015), 2) clarify the model that explains the transformation from sulphide to nonsulphide

Recommended citation

Paradis, S., 2015. Sulphides and nonsulphides of the Prairie Creek district; update on the isotope geochemistry, *in* Paradis, S., ed., Targeted Geoscience Initiative 4: sediment-hosted Zn-Pb deposits: processes and implications for exploration; Geological Survey of Canada, Open File 7838, p. 134-151. doi:10.4095/296328

mineralization, and 3) document the effects of the chemical weathering that results in the formation of the supergene nonsulphide mineralization in periglacial regions and supports textural evidence for the supergene origin of nonsulphide deposits using stable isotope data.

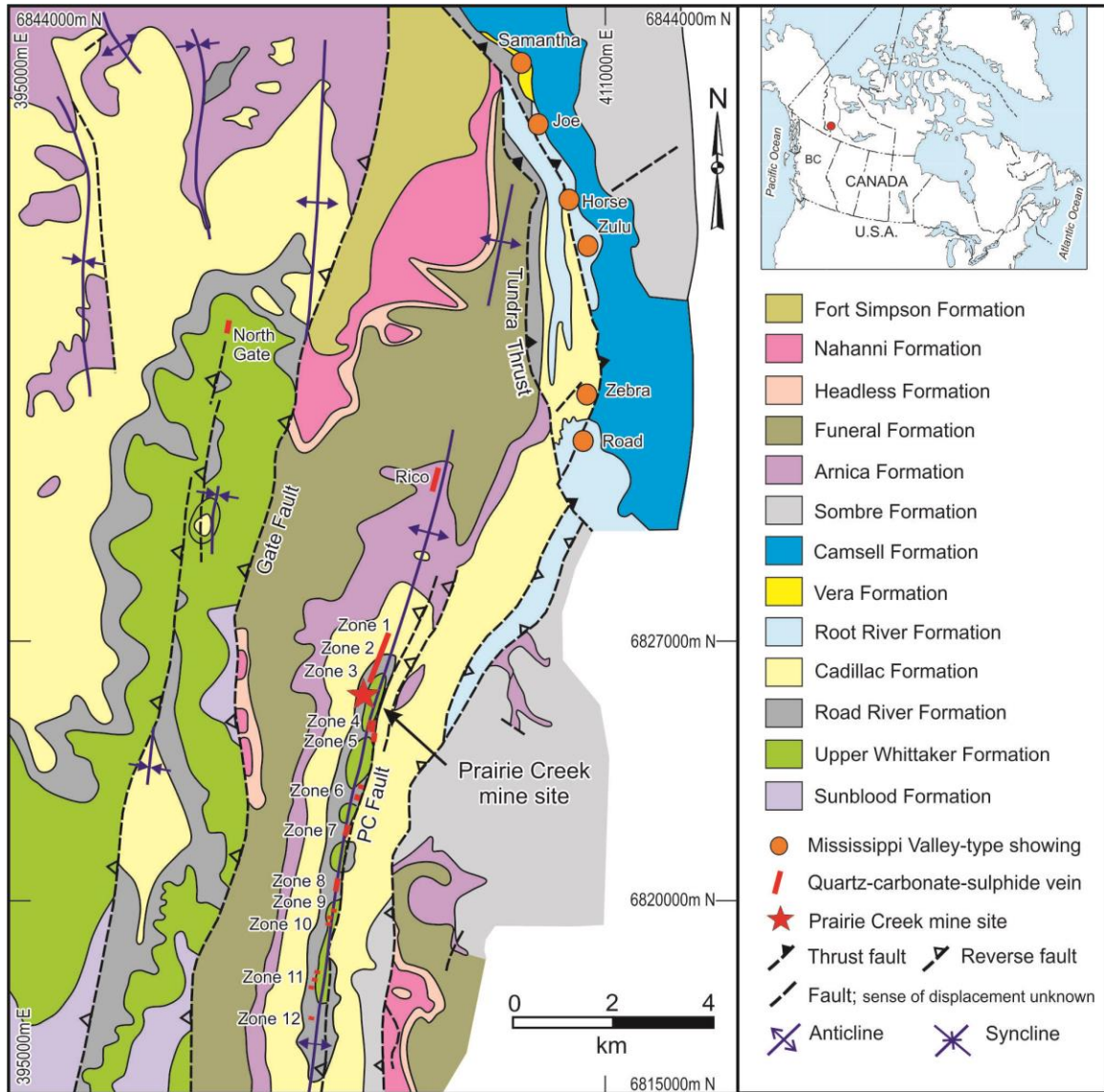


Figure 1. Geological map of the Prairie Creek deposit area showing the quartz-carbonate-sulphide vein system (zones 1 to 12), Rico, and North Gate, location of the mine site at zone 3, and location of the Mississippi Valley-type showings. According to Taylor (1995), the Zebra showing is hosted in a brecciated facies of the Cadillac Formation (i.e. Cadillac ET), which is a facies equivalent to the Root River Formation. The Samantha showing is associated with a 40°-trending and northwest-dipping normal fault, which brings the Vera Formation into contact with the Root River Formation. Note that the stratabound replacement mineralization, which does not outcrop, is not shown on this map (from Morrow and Cook, 1987; Canadian Zinc Corporation, <http://www.canadianzinc.com>).

Physiography, Vegetation and Climate

The Prairie Creek district is located in the Mackenzie Mountains that comprise low mountains (1200-1600m), with moderate to steep flanks and intervening narrow valleys. The Prairie Creek mine site is situated at an elevation of 850 m above mean sea level in an area characterized by an Alpine Forest-Tundra ecoregion of the Boreal Forest. Although located in Canada's north, the Prairie Creek district remained ice free and unaffected by Cordilleran Valley glaciers or the Laurentide Ice Sheet during the Late Pleistocene (Duk-Rodkin, et al., 2007), with the possible exception of meltwater flowing through the area (Duk-Rodkin, personal communication 2014). The Köppen-Geiger classification of the mine site's climate is sub-arctic (Peel et al., 2007). Mean summer and winter temperatures range between 10°C to 14°C and -15°C to -26°C, respectively. Most precipitation falls as rain during the summer months (approximately 300 mm, with total annual precipitation of 500 mm on average).

Geology

The district encompasses the lower to middle Paleozoic northwestern margin of Laurentia, comprising several geographically complex embayments that are inferred to have resulted from differential extension during early to mid-Paleozoic passive-margin subsidence. The Prairie Creek Embayment is located between the Mackenzie Platform and Selwyn Basin, at the transitional zone between basinal and platformal facies deposits. It is a north-south paleo-depression feature where thick accumulations of platformal carbonates and associated deep water basinal rocks occurred. It is bounded to the east by the east-dipping Tundra thrust fault, and 20 km to the west by the west-dipping Manetoe thrust fault (Morrow and Cook, 1987).

Morrow and Cook (1987) and Gordey and Anderson (1993) divided the lower to middle Paleozoic succession of Prairie Creek Embayment into four ascending subdivisions: 1) Sunblood Platform, 2) Mount Kindle-Root River Assemblage, 3) Prairie Creek Assemblage, and 4) Funeral-Headless Assemblage. The Sunblood Platform consists solely of the middle Ordovician shallow water argillaceous limestone and dolostone of the Sunblood Formation. The Late Ordovician to Devonian Mount Kindle-Root River Assemblage, which consists of the Whittaker, Road River, Cadillac, and Root River formations, hosts the sulphide and nonsulphide mineralization of the Prairie Creek district. The Whittaker Formation consists of three lithofacies: middle to upper Ordovician dark grey silty and sandy limestone, middle to upper Ordovician fine-grained quartzite, and upper Ordovician to Silurian laminated dark grey finely crystalline dolostone, which appears on Figure 1. The latter lithofacies is further subdivided into seven subunits (see Paradis, 2007). The Silurian-Devonian Road River Formation comprises a sequence of graptolite-bearing shale and argillaceous bioclastic shaly dolostone conformably overlying the Whittaker Formation. The Silurian-Devonian Cadillac Formation consists of carbonate-rich orange-weathering siltstone. The Silurian Root River Formation is a shelf equivalent of the basinal

facies of the Cadillac Formation, and it consists of light grey vuggy micritic dolostone. The Silurian-Devonian Prairie Creek Assemblage is restricted to a local depression that was filled by the clastic Cadillac Formation and detrital components of the Sombre and Arnica formations. Gradual filling of the Prairie Creek Embayment was followed by deposition of the Funeral-Headless Assemblage marking the return to a simpler shelf to basin transition by the Middle Devonian (Morrow and Cook, 1987; Falck, 2007). For more information on these formations, and those shown on Figure 1 and not mentioned here (i.e. Vera, Camsell, Nahanni and Fort Simpson) see Morrow and Cook (1987).

The dominant structures in the Prairie Creek district are doubly plunging folds (Figure 1) with north-south trending fold axes which are cut by steeply dipping wrench faults that were subsequently rejuvenated as high angle reverse faults (Morrow and Cook, 1987). The reverse faults are post-dated by prominent north-trending nearly flat thrust faults, which occur primarily in the platform carbonates flanking the embayment (Morrow and Cook, 1987), and are related to regional compression during the Laramide Orogeny. Two major thrusts, the Tundra Thrust to the east (Figure 1) and the Manetoe Thrust 20 km to the west (not shown on Figure 1), define the present margins of the Prairie Creek Embayment (Morrow and Cook, 1987). In the immediate area of the Prairie Creek mine site (i.e. zone 3; Figure 1), faulting and folding axes trend north-south, resulting in windows of Road River shales and dolostones of the Whittaker Formation being exposed along the core of the Prairie Creek anticline. The anticline is structurally bounded to the east by the Prairie Creek (PC) Fault and to the west by the Gate Fault. These faults are presently north-south striking, reverse west-dipping (65° to 90°) structures that could have been originally normal faults (Earls, 1995; Fraser, 1996). The Prairie Creek Fault is a steeply dipping reverse fault that is up to 40 m in thickness and has a 1500 m displacement (Morrow and Cook, 1987).

All rocks in the study area have been compacted, lithified during burial, and subjected to increased heat and pressure during the Laramide Orogeny (latest Cretaceous to Eocene; Falck, 2007) and reached a maximum of prehnite-pumpellyite (sub-greenschist) facies). Foliation and cleavage are poorly developed, except in pelitic rocks that are characterized by a slaty cleavage.

Mineralization

The quartz-carbonate-sulphide vein mineralization was discovered in 1928 by Poole Field and was first described by Thorpe (1972). The SRS were discovered by Canadian Zinc Corporation (CZN) in 1992, while surface drilling was being carried out to extend the quartz-carbonate-sulphide vein resources at depth. In 1970, the Samantha showing, the first of the MVT showings was discovered, followed by the Joe showing in 1981 and the other ones in 1993 (Taylor, 1995). For the purpose of this paper, the various types of mineralization are presented and described here as they have been in previous studies (Fraser, 1996; Findlay, 2000; Paradis, 2007; AMC Mining Consultants, 2014).

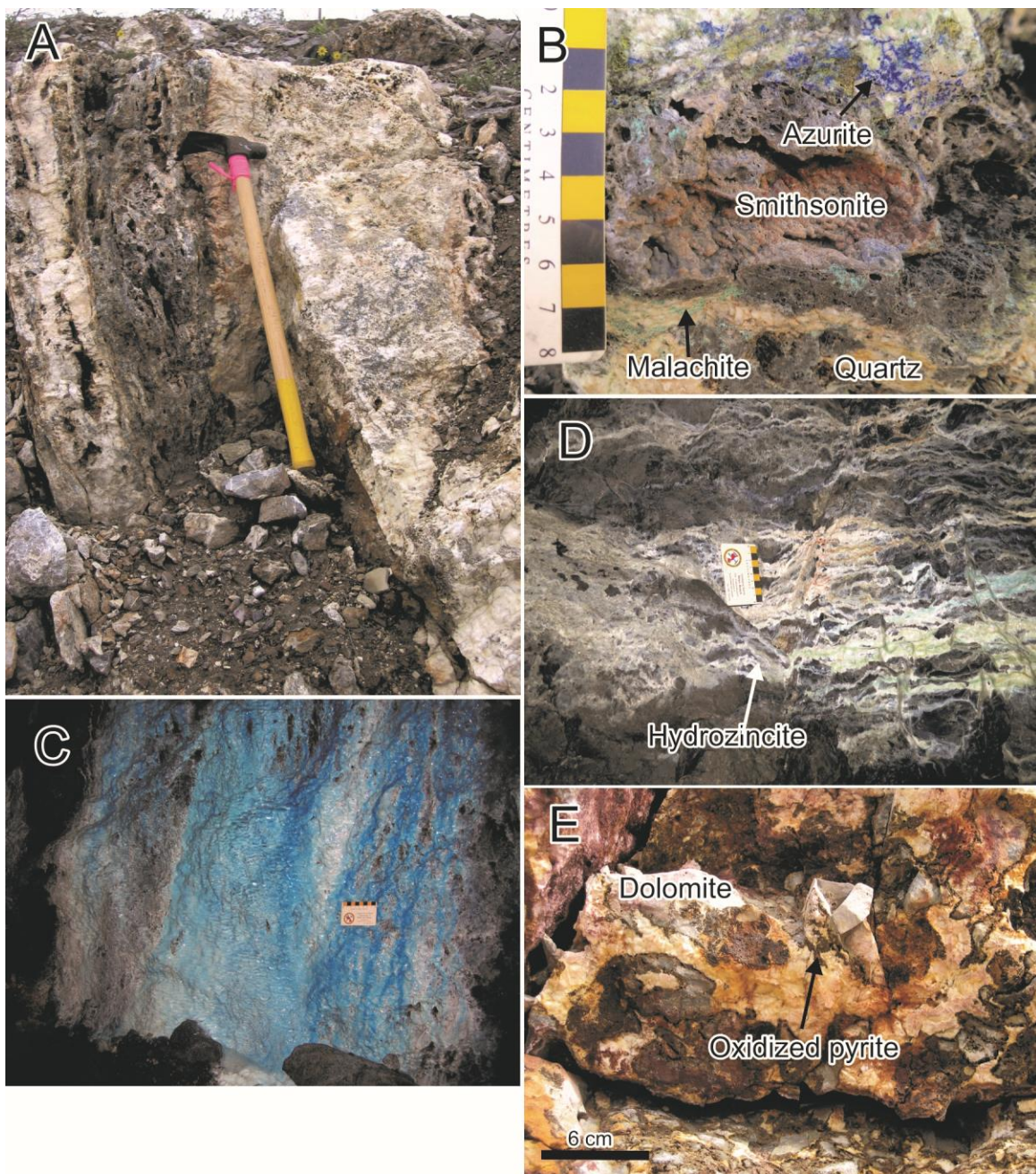


Figure 2. Field photos A) Photograph of the quartz-carbonate-sulphide vein exposure at zone 8 of the Prairie Creek deposit. B) Close-up view of the quartz-carbonate-sulphide vein exposure at zone 8. C) and D) Underground exposures of the quartz-carbonate-sulphide vein at the Mine site (zone 3) showing azurite (C) and hydrozincite (D) precipitating on the walls of the 930 level mine adit. E) Photograph of sparry dolomite filling cavities and oxidized pyrite rimming dolostone fragments at the Zebra showing (Mississippi Valley-type).

Quartz-carbonate-sulphide veins

The quartz-carbonate-sulphide veins are exposed in 12 showings (zones 1 to 12) along a N-S trending 16 km-long corridor (Figure 1). They strike approximately 320 to 360° and dip between 40° east to vertical (Canadian Zinc Corporation, 2010), and fill fractures parallel to regional-scale faults crosscutting the Lower Paleozoic strata (dolostones of the Upper Whittaker Formation, shales of the Road River Formation and dolostones of the Cadillac and Arnica formations) and the SRS. The veins are not folded but they are strongly sheared and brecciated.

The main sulphides within the veins are sphalerite and galena and they are accompanied by lesser concentrations of pyrite and tetrahedrite-tennantite. The sulphides form massive aggregates and disseminations in quartz, calcite, and locally dolomite gangue. In near-surface portions of the veins, sulphides were largely converted to smithsonite, cerussite, azurite, malachite, anglesite, and hydrozincite (Figure 2a, b). Stavinga (2014) and Stavinga et al. (2015) also detected a variety of arsenates [segnitite $\text{PbFe}_3^{3+}\text{H}(\text{AsO}_4)_2(\text{OH})_6$, arsensumebite $\text{Pb}_2\text{Cu}(\text{AsO}_4)(\text{SO}_4)(\text{OH})$, beudantite $\text{PbFe}_3^{3+}(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$, mimetite $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$, adamite $\text{Zn}_2(\text{AsO}_4)(\text{OH})$, duftite $\text{PbCu}(\text{AsO}_4)(\text{OH})$, bayldonite $\text{Pb}(\text{Cu,Zn})_3(\text{AsO}_4)_2(\text{OH})_2$], Pb-Sb-sulphide (bournonite PbCuSbS_3), Pb-Sb-oxide (bindheimite $\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O,OH})$), other sulphides (acanthite Ag_2S , cinnabar HgS , and covellite CuS), Fe-(oxy)hydroxide (goethite $\text{Fe}^{3+}\text{O}(\text{OH})$), and sulphates (barite BaSO_4 , christelite $\text{Zn}_3\text{Cu}_2(\text{SO}_4)_2(\text{OH})_6 \cdot 4\text{H}_2\text{O}$) in minor amounts.

Nonsulphide zones are developed preferentially at the surface but they may extend to depths of 200 m below the surface. Figure 3 illustrates the distribution of $\text{PbO} + \text{ZnO}$ (wt.%) within the quartz-sulphide vein system of zone 3 (Prairie Creek mine site), which reflects the oxidation of the primary sulphides (sphalerite, galena and tetrahedrite-tennantite). At the other zones, the depth of oxidation has not been determined. Within the underground exposures of zone 3, nonsulphides (mainly iron oxides, azurite, hydrozincite, and malachite) are developed along fractures and coat exposed walls (Figure 2c, d). In the underground workings, about 15-20% of the lead sulphides and 10% of the zinc sulphides have undergone oxidation (pHase Geochemistry, 2010) forming mixed ore (as defined by Simandl and Paradis, 2009). At the surface, all sulphides are variously oxidized. Sphalerite alters to smithsonite (Figure 4a, b), which forms spectacular botryoidal growths of many colours (medium to pale green, blue-green, brown, red, orange, yellow-off-white, and colourless) within the vein system. Galena alters to cerussite (Figure 4c, d) and/or anglesite, which form alteration rims. All of these secondary minerals also fill fractures and voids. Goethite replaces pyrite and forms rims around it, or completely pseudomorphoses it. Cerussite, smithsonite, arsenates, and Pb-Sb oxide commonly precipitate along the edges of altered pyrite (Stavinga, 2014). Tetrahedrite-tennantite oxidized mainly into Cu-carbonates (azurite, malachite), arsenates, bindheimite, and christelite (Stavinga, 2014). Several of the oxidation phases derived from tetrahedrite-tennantite coexist with cerussite, smithsonite, and anglesite as inclusions and precipitates along crystal boundaries, or they occur disseminated within the oxidized vein

material. Covellite is locally present as a partial rim around galena, or it can be an intergrowth with anglesite, cerussite, and smithsonite (Figure 4e).

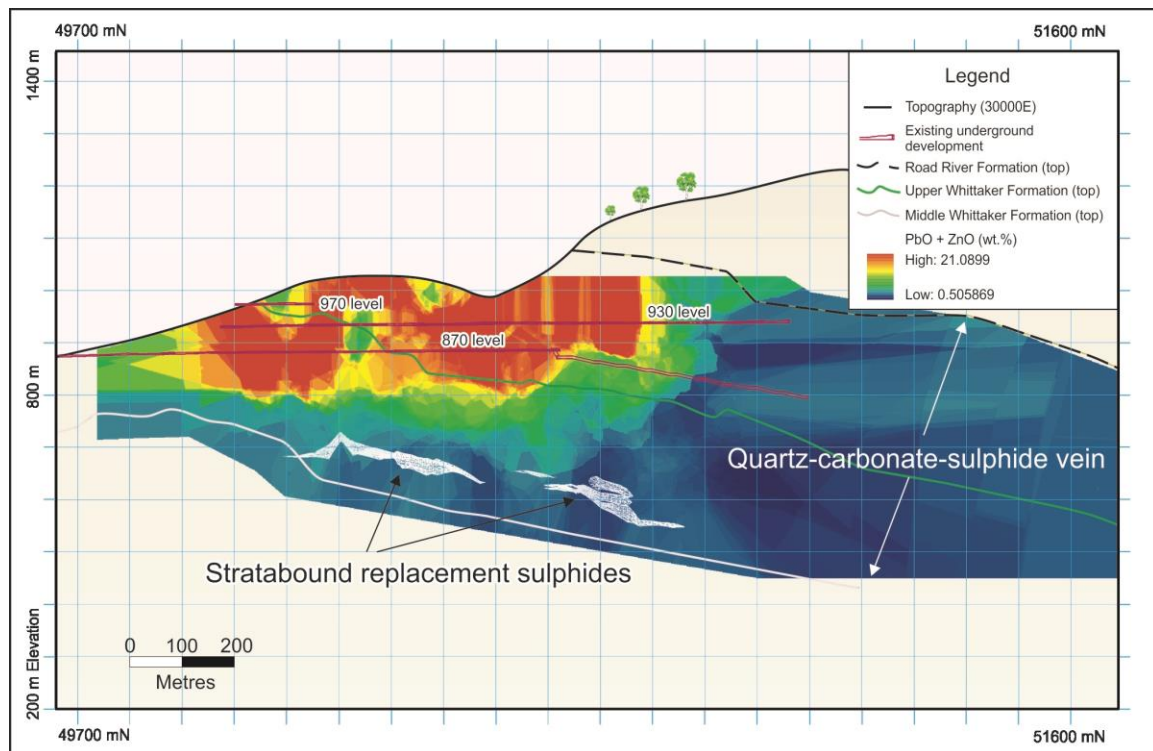


Figure 3. NNE-SSW longitudinal section (viewing along 30000E) illustrating the PbO + ZnO (wt.%) within the quartz-sulphide vein system at the Prairie Creek Mine site (zone 3). The coordinates are in NAD 1983 UTM Zone 10N. Figure was draw by K. Cupit from Canadian Zinc Corporation, and it is included here courtesy of Canadian Zinc Corporation.

Stratabound replacement sulphides (SRS)

The SRS, which do not outcrop, have been located by drilling in zones 3, 4, 5, and 6 along a strike length of more than 3 km. They form lenses replacing various dolostone facies of the Upper Whittaker Formation. The largest lens (SD1) has a minimum lateral dimension of 400 m by 100 m and a maximum thickness of 28 m (Earls, 1995; Findlay, 2000); it preferentially replaces the mottled dolostone unit (OSw3-2; see Paradis, 2007).

The SRS zones consist of pyrite, sphalerite, galena, and trace amount of tetrahedrite-tennantite in a gangue of quartz, dolomite, and calcite. The textures are complex ranging from complete to partial replacement of the dolostone by fine- to coarse-grained massive aggregates of pyrite, yellowish to pinkish sphalerite and galena to fine-grained laminated sulphides to rare open-space cavity-fill textures that resemble MVT style mineralization.

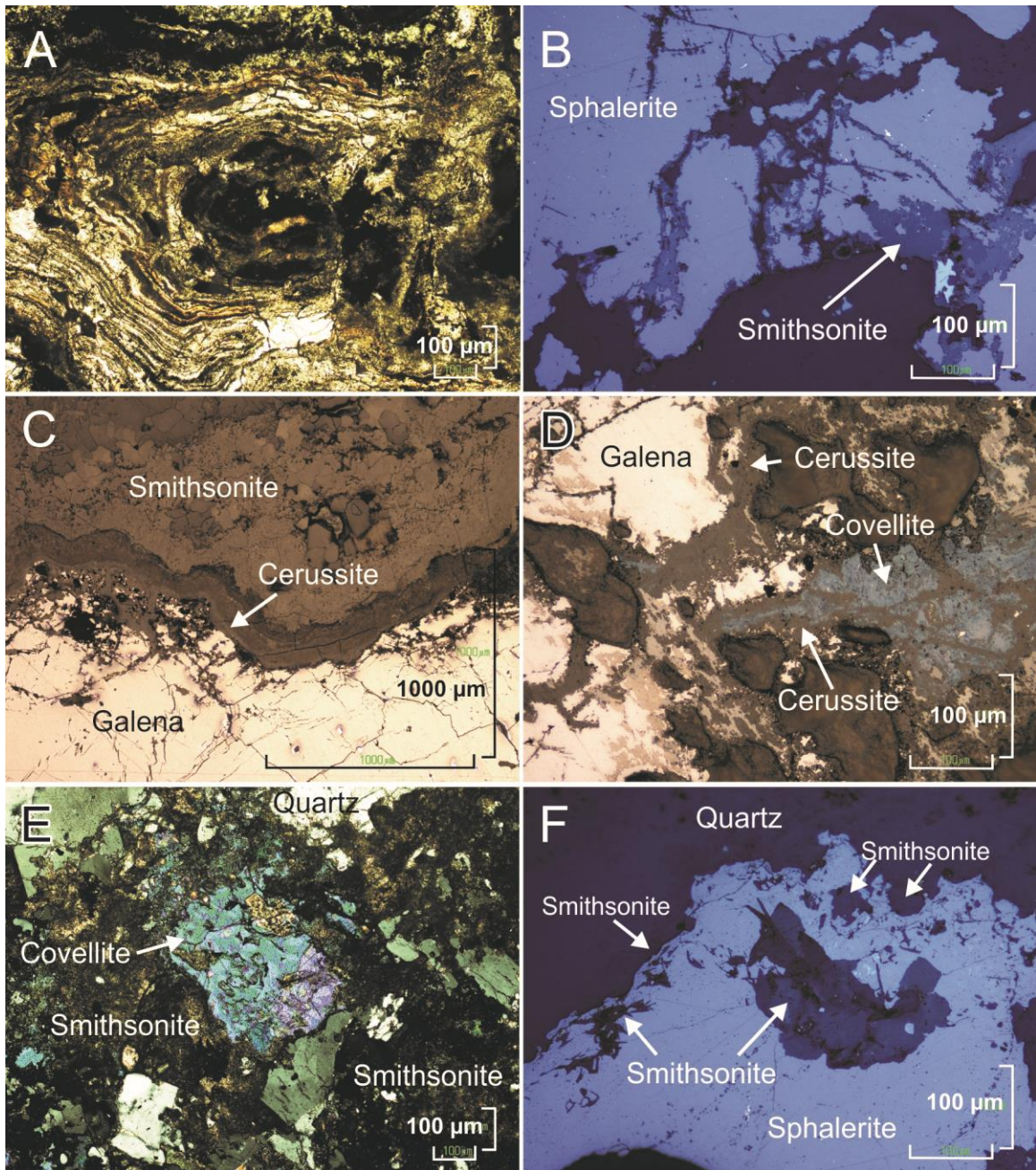


Figure 4. Photomicrographs of the oxide mineralization. A) Botryoidal growths of smithsonite in quartz-carbonate-sulphide vein, sample Z8-S7A, transmitted light. B) Smithsonite altering sphalerite in quartz-carbonate-sulphide vein, sample PCU07-21 at 98.7, reflected light. C) Cerussite forming a rim on galena in quartz-carbonate-sulphide vein, sample Z8-S7A, reflected light. D) Cerussite altering galena and intergrown with covellite in quartz-carbonate-sulphide vein, sample Z8-S7A, reflected light. E) Covellite in groundmass of smithsonite in quartz-carbonate-sulphide vein, sample S8, crossed polars. F) Smithsonite filling cavity in sphalerite and altering it along the edge and fractures of grain in stratabound replacement sulphide zone, sample PC11-209A at 209.67, reflected light.

SRS contain low concentrations of nonsulphide minerals relative to the quartz-carbonate-sulphide veins (Paradis, 2007; Canadian Zinc Corporation, 2010). However, when oxidation is present, it occurs as fracture- and void-fillings, and local replacement of sphalerite, galena, and pyrite. Sphalerite is locally altered to smithsonite along the edges and fractures of the grains (Figure 4f), and galena is partially altered to anglesite and/or cerussite. Pyrite is partially replaced by goethite.

Mississippi Valley-type sulphides

The MVT showings are discontinuously exposed over a distance of approximately 12 km in the coarse biohermal reefs and breccias of the Root River Formation (Figure 1). They are referred to, from north to south, as Samantha, Joe, Horse, Zulu, Zebra and Road showings. They consist of pyrite, sphalerite, and minor galena that form colloform textures rimming dolostone fragments in open-space breccias filled by sparry and saddle white dolomite, and crustiform pyrite-sphalerite veinlets crosscutting the dolostone (Figure 2e). Pyrite is commonly oxidized to hematite/goethite, and sphalerite is locally replaced by smithsonite. Malachite was observed in the trenches of some showings (e.g. Samantha).

Results/Data Analysis

Carbon, Oxygen, and Strontium Isotopes

Analytical Methods

Carbon and oxygen isotope analyses were done on pure carbonate phases at Delta-Lab of the Geological Survey of Canada in Québec City and at the G.G. Hatch Stable Isotope Laboratory of the University of Ottawa. Carbonate mineral species are reacted under vacuum at either 25.0°C or 50.0°C with anhydrous phosphoric acid to release CO₂ (McCrea, 1950). Isotopic ratios are converted by their respective fractionation factors. Results are reported in conventional per mil notation (‰) relative to Vienna Pee-Dee Belemnite (VPDB) and VSMOW standards. Precision, based on replication of international and internal standards, is ±0.1‰ for carbon and oxygen isotope analyses.

Strontium isotope analyses were done by Brian Cousens on dolomite and calcite at the Isotope Geochemistry and Geochronology Research Facility (IGGRF) of Carleton University, and by B. Davis at the geochronology laboratories of the Geological Survey of Canada. Splits of powder samples used for C and O isotope analyses were treated for Sr separation by standard ion exchange techniques. Mass spectrometry was performed on a ThermoFinnigan Triton thermal ionization (TI) mass spectrometer. Isotope ratios were normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.11940$ to correct for fractionation and are presented relative to a value of 0.708043 for the NIST Standard Reference Material, Eimer and Amend (E&A) SrCO₃. Uncertainty in $^{87}\text{Sr}/^{86}\text{Sr}$ is expressed as ±2 sigma of the mean, equivalent to two standard errors (2σ).

Results

Averages of carbon, oxygen, and strontium isotope analyses are presented in Table 1, and the results are illustrated in Figure 5a and b. The complete data set will be published in a separate paper (Paradis et al., 2015b).

Dolostone of the Upper Whittaker Formation has $\delta^{18}\text{O}_{\text{VPDB}}$ and $\delta^{13}\text{C}_{\text{VPDB}}$ values ranging from -10.5 to -5.8‰ and -2.0 to 1.4‰, respectively. Argillaceous dolostone of the Road River Formation form a tight cluster on Figure 5a with $\delta^{18}\text{O}_{\text{VPDB}}$ and $\delta^{13}\text{C}_{\text{VPDB}}$ values ranging from -6.6 to -5.3‰ and -0.6 to 0.4‰, respectively. Dolostone of the Root River Formation have $\delta^{18}\text{O}_{\text{VPDB}}$ values of -7.2 to -5.3‰ and $\delta^{13}\text{C}_{\text{VPDB}}$ values of -1.4 to 1.7‰. The O and C values of these carbonates are similar to those of Ordovician and Silurian marine carbonates obtained by Veizer et al. (1999). Most samples from the Upper Whittaker Formation have $^{87}\text{Sr}/^{86}\text{Sr}$ values higher than 0.7120, which defines the “Maximum Sr Isotope Ratio of Basinal Shale” (MASIRBAS; Machel and Cavell, 1999) in the Cordillera (Figure 5b). They are also higher than Ordovician-Silurian marine carbonates (0.7078-0.7095; Veizer et al., 1999). The one sample from the Root River dolostone and one sample of the Upper Whittaker Formation taken west of the Gate Fault plot below MASIRBAS, similar to values published for the Western Canada Sedimentary Basin (WCSB), Presqu’île barrier, and other dolostones of the northern Rocky Mountains (Paradis, 2007). $^{87}\text{Sr}/^{86}\text{Sr}$ values for the non-mineralized Upper Whittaker dolostone are variable; however they increase in proximity to the SRS mineralization (Fraser, 1996; Paradis, 2007).

Dolomite gangue associated with the SRS has $\delta^{18}\text{O}_{\text{VPDB}}$ values ranging from -6.9 to -14.9‰ and $\delta^{13}\text{C}_{\text{VPDB}}$ values ranging from -4.7 to -2.3‰. These values are lower in $\delta^{13}\text{C}_{\text{VPDB}}$ but similar in $\delta^{18}\text{O}_{\text{VPDB}}$ values (except for two samples with low $\delta^{18}\text{O}_{\text{VPDB}}$ values of -12.2 and -14.9‰) to the host dolostone of the Upper Whittaker Formation. Their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7138 to 0.7239) are similar to the host dolostone of the Upper Whittaker Formation that are in proximity to the stratabound replacement zones. All these values are more radiogenic than Ordovician-Silurian marine carbonates (0.7078-0.7095; Veizer et al., 1999).

Dolomite gangue associated with the quartz-carbonate-sulphide veins has variable $\delta^{18}\text{O}_{\text{VPDB}}$ values of -7.3 to -15.3‰, $\delta^{13}\text{C}_{\text{VPDB}}$ values of 0.3 to -6.3‰, and $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.7096 to 0.7285 (Table 1).

Sparry dolomites associated with MVT showings have $\delta^{18}\text{O}_{\text{VPDB}}$ values ranging from -17.6 to -10.7‰ and $\delta^{13}\text{C}_{\text{VPDB}}$ values ranging from -7.2 to -1.0‰ with a broad co-variance between the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. Their $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.7105 to 0.7127) plot in a small field on Figure 5; they are slightly more radiogenic than Silurian marine carbonates (0.7079-0.7088; Veizer et al., 1999), but they are similar to values of the coarse crystalline dolomite associated with the Manetoe facies in the Mackenzie Mountains, and the MVT Zn-Pb Robb Lake deposit in the northern Rocky Mountains (see Paradis, 2007).

Table 1. Oxygen, carbon, and strontium isotope values, Prairie Creek district, NT.

	$\delta^{13}\text{C}_{(\text{VPDB})}$	$\delta^{18}\text{O}_{(\text{VPDB})}$	$\delta^{18}\text{O}_{(\text{VSMOW})}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Dolostone of the Whittaker Formation				
Number of samples	36	36	36	9
Range	-2.0 to 1.4	-10.5 to -5.8	20.1 to 24.9	0.7096 to 0.7267
Average	-0.1	-8.2	22.5	0.7191
Standard deviation	0.7	1.3	1.3	0.0057
Argillaceous dolostone of the Road River Formation				
Number of samples	5	5	5	
Range	-0.6 to 0.4	-6.6 to -5.3	24.0 to 25.4	-
Average	0.2	-6.2	24.5	-
Standard Deviation	0.4	0.5	0.6	-
Dolostone of the Root River Formation				
Number of samples	8	8	8	1
Range	-1.4 to 1.7	-7.2 to -5.4	23.4 to 25.3	0.7093
Average	0.8	-6.1	24.5	0.7093
Standard Deviation	1.0	0.7	0.7	-
Dolomite gangue associated with stratabound replacement sulphides				
Number of samples	15	15	15	11
Range	-4.7 to -2.3	-14.9 to -6.9	15.5 to 23.8	0.7138 to 0.7239
Average	-3.0	-8.9	21.7	0.7184
Standard Deviation	0.6	2.1	2.2	0.0035
Dolomite gangue associated with quartz-carbonate-sulphide veins				
Number of samples	4	4	4	3
Range	-6.3 to 0.3	-15.3 to -7.3	15.2 to 23.4	0.7096 to 0.7252
Average	-3.1	-12.3	18.2	0.7211
Standard Deviation	2.7	3.6	3.7	0.0101
Dolomite gangue associated with Mississippi Valley-type deposits				
Number of samples	10	10	10	6
Range	-7.2 to -1.0	-17.6 to -10.7	12.7 to 19.8	0.7105 to 0.7127
Average	-3.3	-14.6	15.9	0.7117
Standard Deviation	1.9	2.1	2.1	0.0009
Smithsonite associated with quartz-carbonate-sulphide veins				
Number of samples	14	14	14	1
Range	-5.8 to -3.5	-16.7 to -15.1	13.6 to 15.3	0.7254
Average	-4.5	-16.0	14.3	-
Standard Deviation	1.0	0.9	0.9	-
Cerussite				
Number of samples	1	1	1	
Range	-8.6	-16.8	13.5	-

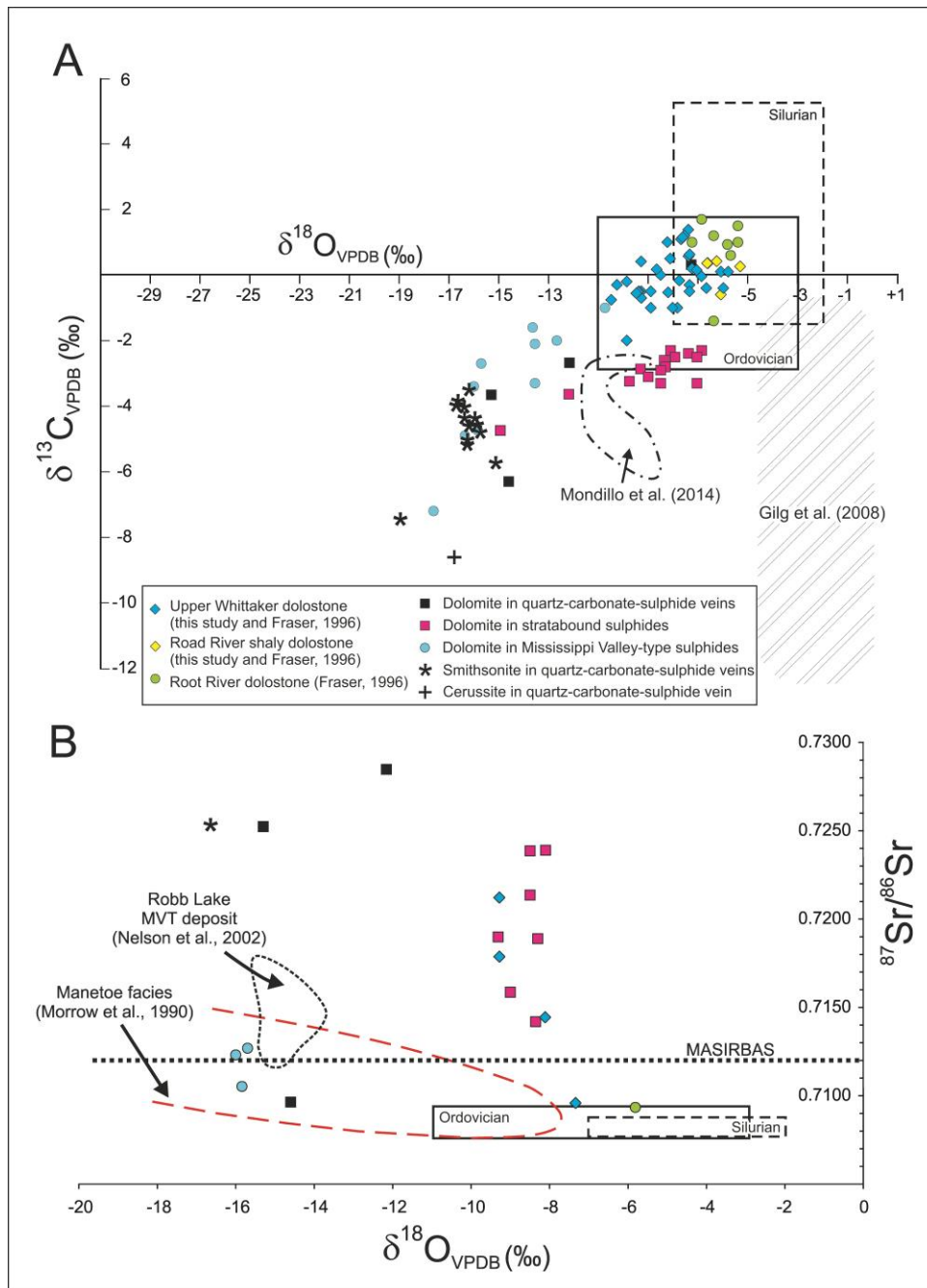


Figure 5. A) Plot of $\delta^{18}\text{O}_{\text{VPDB}}$ and $\delta^{13}\text{C}_{\text{VPDB}}$ values of the host dolostones, and dolomite, smithsonite, cerussite associated with SRS, quartz-carbonate-sulphide veins, and MVT mineralization. The fields for supergene smithsonite from the Jabali deposit (Yemen; Mondillo et al., 2014) and from the compilation of Gilg et al. (2008) are shown for comparison. B) $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\delta^{18}\text{O}_{\text{VPDB}}$. Fields of Ordovician and Silurian marine carbonate values are from Veizer et al. (1999). The fields for coarsely crystalline dolomite associated with the Robb Lake Zn-Pb MVT deposit in the northern Rocky Mountains and the Manetoe hydrothermal facies in the Mackenzie Mountains are shown for comparison. Maximum Sr isotope ratio of basal shale (MASIRBAS) is from Machel and Cavell (1999).

Smithsonite samples from the quartz-carbonate-sulphide veins have a narrow range of $\delta^{18}\text{O}_{\text{VPDB}}$ values (-16.7 to -15.1‰) and $\delta^{13}\text{C}_{\text{VPDB}}$ values of -5.8 to -3.5‰. One sample that consists of a mixture of smithsonite and cerussite has $\delta^{18}\text{O}_{\text{VPDB}}$ value of -18.9‰ and $\delta^{13}\text{C}_{\text{VPDB}}$ values of -7.5‰. The $\delta^{18}\text{O}_{\text{VPDB}}$ and $\delta^{13}\text{C}_{\text{VPDB}}$ ratios of a single cerussite sample (courtesy of Drew Stavinga) are -16.9‰ and -8.6‰, respectively. One smithsonite sample has a $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7254.

Models/Discussion

Prairie Creek district is unusual because it hosts 3 types of carbonate-hosted Zn-Pb-Ag deposits (veins, SRS and MVT). Outcropping and near-surface portions of the vein and MVT sulphides have undergone extensive oxidation with the precipitation of smithsonite, cerussite, azurite, malachite, and anglesite as the main nonsulphide minerals. Other secondary metal carbonates, arsenates, and sulphides are present as accessories (Stavinga, 2014). Oxidation is not as well developed in the SRS compared to the veins and MVT deposits because the SRS lenses occur at depth (on average more than 200 m below the surface).

The age of the oxidation process is uncertain, but indirect geological evidences suggest that it may have started forming after the Laramide Orogeny (latest Cretaceous to Eocene) and is still ongoing. Nonsulphides worldwide typically formed between 11°C to 35°C (Boni et al., 2003; Gilg et al., 2008), in warm to temperate climatic conditions. Several warmer climatic periods (warmer than today) occurred during the Cenozoic (Lower Oligocene and Lower to Middle Miocene, Pliocene, and Holocene) providing conditions that were favourable for supergene oxidation of sulphides. It has been suggested that nonsulphide deposits in southern and central British Columbia (BC) started forming before or slightly after the last glacial maximum (~14,500 ^{14}C yr BP), with the best climatic conditions occurring around 10,000–7,000 ^{14}C yr BP (Paradis et al., 2011; Paradis et al., 2015a). Similar ages have been postulated for supergene nonsulphide deposits in the northern Canadian Cordillera with ^{14}C dating of the supergene Zn deposit at Howards Pass, Yukon, established to be younger than 9610 ± 100 ^{14}C yr BP, i.e. Holocene in age (Jonasson et al., 1983). This can also be the case for the nonsulphide minerals at Prairie Creek. Additionally, the Prairie Creek district seems to have escaped the last glaciation events during the Late Pleistocene (Duk-Rodkin, personal communication, 2014), and this would explain the excellent preservation of the nonsulphide zones.

The C and O isotopic composition of unaltered dolostones of the Upper Whittaker dolostone, Root River shaly dolostone and Road River dolostone form overlapping clusters within the field of Ordovician carbonates (Figure 5a) in agreement with a sedimentary origin. Dolomite gangue from Mississippi Valley-type deposits form a trend originating in the field of Ordovician carbonates and showing progressively lower $\delta^{18}\text{O}_{\text{VPDB}}$ and $\delta^{13}\text{C}_{\text{VPDB}}$ ratios. Dolomites from the quartz-carbonate-sulphide veins also plot along this trend, and those from the stratabound replacement sulphide zones follow a similar trend. These trends suggest that dolomite gangue formed from fluids that equilibrated with the host

rocks. With the exception of two samples, gangue dolomite from SRS has the same $\delta^{18}\text{O}_{\text{VSMOW}}$ values as the Upper Whittaker dolostone, but lower $\delta^{13}\text{C}_{\text{VPDB}}$ values, which indicate a mixed contribution of inorganic carbon from the Whittaker dolostone and another source. Smithsonite and cerussite from the quartz-carbonate-sulphide veins have negative $\delta^{18}\text{O}_{\text{VSMOW}}$ and $\delta^{13}\text{C}_{\text{VPDB}}$ values (Figure 5a), coinciding with the most negative $\delta^{18}\text{O}_{\text{VPDB}}$ and $\delta^{13}\text{C}_{\text{VPDB}}$ of the dolomites from the mineralized veins confirming that the supergene fluids gradually equilibrated with the carbonate-hosted mineralized veins. Smithsonite from quartz-carbonate-sulphide veins at Prairie Creek has lower $\delta^{18}\text{O}_{\text{VSMOW}}$ values than those of supergene smithsonite worldwide (compilation of Gilg et al., 2008; and data of Mondillo et al., 2014) but their $^{13}\text{C}_{\text{VPDB}}$ values overlap (Figure 5a). The narrow range in $\delta^{18}\text{O}_{\text{VSMOW}}$ values of smithsonite from Prairie Creek is characteristic of supergene smithsonite worldwide and indicates equilibration with meteoric waters (Gilg et al., 2008). It also suggests a constant formation temperature and a single meteoric fluid source. The wide range of $\delta^{13}\text{C}_{\text{VPDB}}$ values are explained by a different provenance of the carbon within the supergene fluids. In the Prairie Creek case, $\delta^{13}\text{C}$ values indicate a contribution of inorganic carbon from the host rock carbonates.

Using the oxygen isotope fractionation equation for water and smithsonite of Gilg et al. (2008):

$$\ln \alpha_{\text{smithsonite-water}} = 3.10 (10^6/T^2) - 3.50$$

the calculated formation temperature of smithsonite can be approximated. Precipitated water in northern Canada is strongly depleted in ^{18}O because water vapor in high latitudes contains less ^{18}O as a result of preferential rainout of the heavy isotope during the transfer of air masses from low to high latitudes (Rozanski et al., 1993; Bowen and Wilkinson, 2002; Delavau et al., 2011). In Yellowknife, for example, present day's annual $\delta^{18}\text{O}_{\text{VSMOW}}$ value is $\sim -21.2\text{‰}$ with average values around -16.4‰ in summer and -24‰ in winter [Canadian Network for Isotopes in Precipitation (CNIP) database]. This high variability in $\delta^{18}\text{O}_{\text{VSMOW}}$ values is strongly dependent on temperature, as the sub-arctic region is subjected to strong temperature contrasts between summer (10°C to 14°C and winter months (-15°C to -26°C). If we use the average $\delta^{18}\text{O}_{\text{VSMOW}}$ value of -21.2‰ for the meteoric water, calculated precipitation temperature for the smithsonite would be around 9°C , which is low compare to typical precipitation temperatures of nonsulphides worldwide (11°C to 23°C , Gilg et al., 2008; 20°C to 35°C ; Boni et al., 2003), but comparable to temperatures obtained for the precipitation of supergene smithsonite at the Reef Creek deposit in Alaska (Santoro et al., 2014). If we assume that smithsonite (and the other nonsulphides) precipitated during the summer months, the calculated precipitation temperatures are around 29°C , which is also realistic for supergene minerals precipitating in the vadose zone. If the nonsulphides started forming immediately after the Laramide orogeny at around 55 Ma, the average $\delta^{18}\text{O}_{\text{VSMOW}}$ values of the meteoric waters would be less negative due to warmer climate than today, and the resulting temperature of formation could be higher than 29°C . This supports the hypothesis that nonsulphides can form and be preserved in the sub-

arctic regions of Canada. Overall, the absence of glaciation favours preservation of the nonsulphide mineralization; but nonsulphide deposits with favourable morphology and orientation would survive the glaciation regardless (Simandl and Paradis, 2009). Other glaciated areas in the world previously regarded as unfavourable may be prospective for nonsulphide deposits.

Implications for Exploration

The characterization of the carbonate-hosted nonsulphide Zn-Pb deposits is essential for the formulation of integrated exploration programs targeting these deposits across Canada, and for understanding and facilitating eventual mineral processing. Zinc or lead oxides, silicates and carbonates are direct indicators for nonsulphide base metal deposits and indirect indicator minerals in exploration for MVT, SEDEX, Irish-type, and vein-type Zn-Pb deposits.

Most of the supergene nonsulphide deposits in the world formed in warm to temperate climate conditions (Boni et al., 2003; Hitzman et al., 2003), and only a few formed in arid environments (Namibia and Iran, Reichert and Borg, 2008). Until recently, it was believed that nonsulphide minerals could not form in cold and wet climatic conditions. Examples in BC (Salmo and Quesnel districts; Paradis et al., 2011, 2015a), Yukon (Howards Pass; Jonasson et al., 1983), Alaska (Reef Creek; Santoro et al., 2014 and now the Northwest Territories (Prairie Creek), disprove this hypothesis.

Future Work

This research gives some insight into the genesis of nonsulphides at Prairie Creek. It complements the geochemical work of Stavinga et al. (2015) and the sulphur isotopic work of Taylor et al. (2015). However, the lack of radiometric ages on the sulphide and nonsulphide deposits limits our ability to refine the genetic models for the deposit-types of the Prairie Creek district. Nonsulphide minerals can be used as indicators in exploration for base metal deposits. Their resistance to transportation and their dispersion trains should be characterized.

Acknowledgements

I am extremely grateful to all personnel of Canadian Zinc Corporation and more specifically to Alan Taylor and Kerry Cupit who provided invaluable geological information on the Prairie Creek deposit and its district. Canadian Zinc Corporation is also thanked for giving us access to the property, allowing us to sample the drill cores and providing pertinent geological information.

References

- AMC Mining Consultants (Canada) Ltd., 2014, Prairie Creek property, Northwest Territories, Canada: Technical Report for Canadian Zinc Corporation. [Online] Available at: <http://www.canadianzinc.com/projects/prairie-creek> [Accessed 01-12-2014].
- Boni, M., Gilg, H., Aversa, G., and Balassone, G., 2003, The "Calamine" of SW Sardinia (Italy): geology, mineralogy and stable isotope geochemistry of a

- supergene Zn-mineralization: *Economic Geology*, v. 98, p. 731–748.
- Bowen, G.J., and Wilkinson, B., 2002, Spatial distribution of $\delta^{18}\text{O}$ in meteoric precipitation: *Geology*, v. 30, p. 315–318.
- Canadian Zinc Corporation, 2010, <http://www.canadianzinc.com/>
- Canadian Network for Isotopes in Precipitation (CNIP)
<http://www.science.uwaterloo.ca/~twdedwar/cnip/cniphome.html>
- Delavau, D., Stadnyk, T., and Birks, J., 2011, Model based spatial distribution of Oxygen-18 isotopes in precipitation across Canada: *Canadian Water Resources Journal*, v. 36 (4), p. 313-330.
- Duk-Rodkin, A., Huntley, D., and Smith, R., 2007, Quaternary geology and glacial limits of the Nahanni National Park Reserve and adjacent areas, Northwest Territories, Canada, *in* Wright, D.F., Lemkow, D., Harris, J.R., ed., Mineral and energy resource assessment of the Greater Nahanni Ecosystem under consideration for the expansion of the Nahanni National Park Reserve, Northwest Territories: Geological Survey of Canada, Open File 5344, p. 125-129.
- Earls, G., 1995, A review of the Prairie Creek deposit, Northwest Territories, Canada: Internal Report, San Andreas Resources Corporation, 36 p.
- Falck, H., 2007, A review of the bedrock geology of the Nahanni River region and its context in the Northern Cordillera, *in* Wright, D.F., Lemkow, D., Harris, J.R., ed., Mineral and Energy Resource Assessment of the Greater Nahanni Ecosystem Under Consideration for the Expansion of the Nahanni National Park Reserve, Northwest Territories: Geological Survey of Canada, Open File 5344, p. 327-365.
- Findlay, A., 2000, Geology and exploration potential of the stratabound replacement massive sulphides, Prairie Creek Mine, Northwest Territories: Internal Report, Canadian Zinc Corporation, 17 p.
- Fraser, S.C., 1996, Geology and Geochemistry of the Prairie Creek Zn, Pb, Ag deposits, Southern Mackenzie Mountains, Northwest Territories: Unpublished M.Sc. thesis, University of Alberta, Edmonton, Alberta, Canada, 146 p.
- Gilg, H. A., Boni, M., Hochleitner, R., and Struck, U., 2008, Stable isotope geochemistry of carbonate minerals in supergene oxidation zones of Zn–Pb deposits: *Ore Geology Reviews*, v. 33, p. 117–133.
- Gordey, S.P. and Anderson, R.G., 1993, Evolution of the Northern Cordilleran Miogeocline, Nahanni map area (105I), Yukon and Northwest Territories: Geological Survey of Canada, Memoir 428, 214 p.
- Hitzman, M.W., Reynolds, N.A., Sangster, D.F., Cameron, R.A., and Carman, C.E., 2003, Classification, genesis, and exploration guides for nonsulfide zinc deposits: *Economic Geology*, v. 98, p. 685–714.
- Jonasson, I.R., Jackson, L.E., and Sangster, D.F., 1983, A Holocene zinc orebody formed by supergene replacement of mosses: *Journal of Geochemical Exploration*, v. 18, p. 189–194.
- Machel, H.G. and Cavell, P.A., 1999, Low-flux, tectonically-induced squeegee fluid flow (“hot flash”) into the Rocky Mountain foreland basin: *Canadian Petroleum Geology, Bulletin* v. 47, p. 510-533.
- McCrea, J. M., 1950, On the isotopic chemistry of carbonates and a

- paleotemperature scale: *Journal of Chemical Physics*, v. 18, p. 849-857.
- Mondillo, N., Boni, M., Balassone, G., Joachimski, M., and Mormone, A., 2014, The Jabali nonsulfide Zn–Pb–Ag deposit, western Yemen: *Ore Geology Reviews*, v. 61, p. 248–267.
- Morrow, D.W. and Cook, D.G., 1987, The Prairie Creek Embayment and Lower Paleozoic strata of the southern Mackenzie Mountains: Geological Survey of Canada, Memoir 412, 195 p.
- Paradis, S., 2007, Isotope geochemistry of the Prairie Creek carbonate-hosted zinc-lead-silver deposit, southern Mackenzie Mountains, Northwest Territories, *in* Wright, D.F., Lemkow, D., Harris, J.R., ed., Mineral and energy resource assessment of the Greater Nahanni Ecosystem under consideration for the expansion of the Nahanni National Park Reserve, Northwest Territories: Geological Survey of Canada, Open File 5344, p. 131-176.
- Paradis, S., Keevil, H., Simandl, G.J. and Raudsepp, M., 2011, Geology and mineralogy of carbonate-hosted nonsulphide Zn-Pb mineralization in southern (NTS 082F/03) and central (NTS 093A/14E, 15W) British Columbia, *in* Geoscience BC Summary of Activities 2010: Geoscience BC, Report 2011-1, p. 143–168.
- Paradis, S., Keevil, H., Simandl, G.J., and Raudsepp, M., 2015a, Carbonate-hosted nonsulphide Zn-Pb mineralization of southern British Columbia, Canada: *Mineralium Deposita*, in press.
- Paradis, S., Taylor, B., Stavinga, D.B., and Falck, H., 2015b, Carbonate-hosted Zn-Pb deposits of the Prairie Creek district, Northwest Territories, Canada; unusual sulphide and nonsulphide mineralization in an embayment of the Selwyn Basin, in preparation.
- Peel, M. C., Finlayson, B. L., McMahon, T. A., 2007, Updated world map of the Koppen- Geiger climate classification: *Hydrology and Earth system sciences*, v. 11, p. 1634-1644.
- pHase Geochemistry, 2010, Geochemical characterization of paste and paste components, Prairie Creek project, Northwest Territories, Canada: Appendix 4 of Developer's Assessment Report, Canadian Zinc Corporation submission to Mackenzie Valley Review Board Environmental Assessment of Prairie Creek Mine EA 0809-002.
- Reichert, J., and Borg, G., 2008, Numerical simulation and geochemical model of supergene carbonate-hosted non-sulphide zinc deposits: *Ore Geology Reviews*, v. 33, p. 134–151.
- Rozanski, K., Araguas-Araguas, L., and Gonfiantini, R., 1993, Isotopic patterns in modern global precipitation, *in* Swart, P.K., et al., ed., *Climate change in continental isotopic records: American Geophysical Union Geophysical Monograph 78*, p. 1–36.
- Santoro, L., Boni, M., Woodman, J., 2014, The Reef Ridge supergene nonsulfide zinc mineralization, Alaska [abs.]: 21st General Meeting of the International Mineralogical Association, Johannesburg, South Africa.
- Simandl, G.J., and Paradis, S., 2009, Carbonate-hosted, nonsulphide, zinc-lead deposits in the southern Kootenay arc, British Columbia (NTS 082F/03), *in* Geological Fieldwork 2008, British Columbia Ministry of Energy and Mines,

- Paper 2009-1, p. 205–218.
- Stavinga, D.B., 2014, Trace element geochemistry and metal mobility of oxide mineralization at the Prairie Creek Zn-Pb-Ag deposit, Northwest Territories: unpublished M.Sc. thesis, Queen's University, Kingston, Ontario, Canada, 153 p.
- Stavinga, D.B., Jamieson, H., Paradis, S., and Falck, H., 2015, Geochemical and mineralogical controls on metal(loid) mobility in the Oxide Zone at Prairie Creek, Northwest Territories, *in* Paradis, S., ed., Targeted Geoscience Initiative 4: Sediment-hosted Zn-Pb deposits: processes and implications for exploration: Geological Survey of Canada, Open File 7838, p. 173-187.
- Taylor, A.B., 1995, Geological Summary of the Northern Sector Pb-Zn Trend on the Prairie Creek property, Northwest Territories; Internal report, San Andreas Resources Corporation, 31 p.
- Taylor, B.E., Paradis, S., Falck, H., and Wing, B., 2015, In situ sulphur isotope study of the Prairie Creek deposit, southern Mackenzie Mountains, Northwest Territories: Deciphering the conundrum of three deposit styles in one, *in* Paradis, S., ed., Targeted Geoscience Initiative 4: Sediment-hosted Zn-Pb deposits: processes and implications for exploration: Geological Survey of Canada, Open File 7838, p. 96-133.
- Thorpe, R.I., 1972, Mineral exploration and mining activities, mainland Northwest Territories, 1966 to 1968; Geological Survey of Canada, Paper 70-70, 139 p.
- Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G.A.F., Diener, A., Ebner, S., Godderis, Y., Jasper, T., Korte, C., Pawellek, F., Podlaha, O.G., and Strauss, H., 1999, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ evolution of Phanerozoic seawater: *Chemical Geology*, v. 161, p. 59-88.