Semi-metal and base metal mobility in the metasedimentary contact aureole surrounding the Dublin Gulch reduced intrusion-related gold system (RIRGS), Yukon, Canada

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Abstract. Precious, semi-, and base metals have been shown to be mobilised from metasedimentary rocks during prograde metamorphism. These form an important source of metals for orogenic gold systems. Similar metal enrichments are observed in reduced intrusion-related gold systems (RIRGS) hosted in the Selwyn basin area. However, no assessment has previously been attempted to determine whether prograde metamorphism of the surrounding metasediments could represent an important metals source for RIRGS. In this study, we focus on the availability and mobilisation of semi- and base metals through mineral reactions occurring in the contact aureole around the Dublin Gulch RIRGS. Pyrite and chlorite are observed in the regionally metamorphosed rocks dominating the semi- and base metals budget. During contact metamorphism, these recrystallise to pyrrhotite and chalcopyrite, and biotite, respectively. These mineral phases contain significantly lower concentrations of metals, compared to their precursor minerals (except Cu and Zn in chalcopyrite). Whole rock geochemistry shows that relative to the contact metamorphosed rocks, the regionally metamorphosed rocks are enriched in As, Sb, Te, Bi, Pb, Zn, and H_2O. This suggests, mobilisation of these elements has occurred, possibly as a metal-rich fluid that could provide an alternative or additional metal source for RIRGS.

1 Introduction

Marine clastic metasedimentary rocks have been the focus of several recent studies (e.g., Pitcairn et al, 2006, 2010 2014; Large et al, 2011, 2012; Hammerli et al, 2016; Thomas et al, 2011; Cave et al, 2015, 2016) on local- and regional- scale trace element mobility associated with regional or contact prograde metamorphic events.

Mineralogical changes with prograde metamorphism are crucial in explaining the mobilisation of trace elements. In the studies of the Otago and Alpine schists, diagenetic or detrital metal-rich mineral phases recrystallise with prograde metamorphism [pyrite to pyrrhotite: Au, As, Ag, Hg, Sb and Mo (Pitcairn et al, 2006, 2010, 2014; Large 2012); rutile to titanite: W (Cave et al, 2015, 2016)]. During this recrystallisation a significant proportion of these metals have been shown to be released into concurrently developing metamorphic fluids that can subsequently be structurally focused to form orogenic gold systems (e.g., Pitcairn et al, 2006, 2010 2014; Large et al, 2011, 2012; Hammerli et al, 2016; Thomas et al, 2011; Cave et al, 2016).

The same prograde mineral recrystallisation reactions are observed in the Selwyn basin area, in contact aureoles associated with reduced intrusion-related gold systems (RIRGS) (e.g., Maloof et al, 2001). This class of deposit forms an important source for global gold, and area also enriched in significant quantities of other metals, including W, As, Te, Sb, Bi, Pb, and Zn (Maloof et al, 2001). Metal source models for RIRGS predominantly suggest metals are derived from the same source regions as the magmas (e.g., Hart et al, 2004). However, the potential that contact metamorphism could provide a significant amount of these metals to RIRGS has not been assessed. In addition, the assimilation of country rock metasediments has been shown to introduce semi- and base metals into magmas (e.g., Samalens et al, 2017), and may provide an additional or alternative source for these metals to RIRGS. This study, aims to establish the framework for future work to address this. Critical to this is understanding metal availabilities in the metasediments. The Yusezyu Formation of the Selwyn basin area, north western Canada (Fig. 1) provides an excellent natural laboratory in which to test this hypothesis. With the Yusezyu Formation hosting numerous RIRGS, being accessible for study, and importantly simplifying this study to one formation.

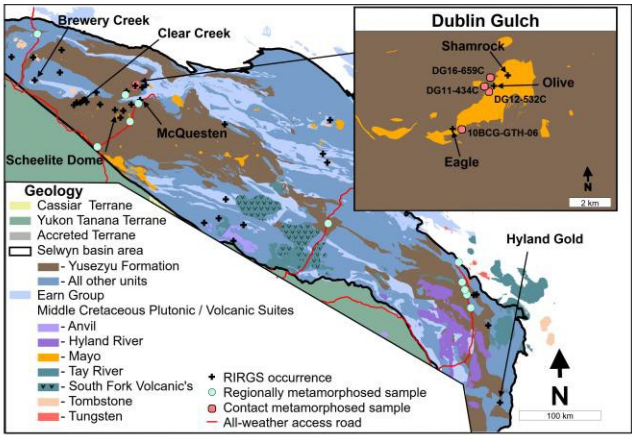

Figure 1. Geological map of the Selwyn basin area (outlined in heavy black) and selected adjacent terranes.

2 Geological setting

The Selwyn basin area (Fig 1) is an extensive Neoproterozoic to Siluro-Devonian continental margin basin that developed on the western margin of Ancestral North America (Gordey and Andersen, 1993). Comprised of a thick (up to 6.65 km) sequence of variably metamorphosed Neoproterozoic to Siluro-Devonian turbiditic metasandstones, shales, and limestones (Gordey and Anderson, 1993; Murphy, 1997). Stratigraphy in the Selwyn basin area is divisible into two groups and seven formations. These are, the Neoproterozoic to Lower Cambrian Hyland Group (Yusezyu, Algae Lake, and Narchilla formations), the Lower Cambrian Gull Lake Formation, the Cambro-Ordovician Rabbitkettle Formation, and the Ordovician-Silurian Road River Group (Duo Lake and Steel Formations) (Gordey and Andersen, 1993). Unconformably overlying the Selwyn basin stratigraphy, and included here in the Selwyn basin area stratigraphy, is the Devono-Mississippian Earn Group (Gordey and Andersen, 1993).

Rocks of the Selwyn basin area are part of the Selwyn fold belt, a domain deformed and metamorphosed (sub-greenschist to middle greenschist facies) during the Jurassic-Cretaceous period, as a response to the accretion of the Yukon- Tanana to the continental margin (Mair et al, 2006). Numerous post-tectonic, mainly mid-Cretaceous (96–90 Ma; Hart et al, 2004) granitic plutons (e.g., the Tay River, and Tombstone suites) intrude the Selwyn basin area. Compositionally these plutons vary, however, an overall trend of subalkalic and weakly to strongly alkalic intrusions is recognised in the western to southern and northern and eastern Selwyn basin area, respectively (Rasmussen et al, 2010). These correspond to the Hyland-Anvil and Tay River suites in the western to southern Selwyn basin area, and the Tungsten, Mayo, and Tombstone suites in the northern and eastern Selwyn basin area (Rasmussen et al, 2010). Around these mid-Cretaceous plutons, contact aureoles are developed that overprint regional structures and metamorphic isograds.

Associated with these intrusions are numerous RIRGS that are observed throughout the Selwyn basin area. These RIRGS form the eastern portion of the globally significant Tintina Gold Belt (TGB). Past production and *in situ* resources from placer and hard rock deposits in the TGB exceeds 1700 tonnes of Au. Dublin Gulch is the most significant RIRGS in the Selwyn basin area, containing constrained in-pit resources of 100 tonnes Au (at 0.63 g/t) (Victoria Gold Corp, 2016). Mineralisation at Dublin Gulch, is typical of many RIRGS in the Selwyn basin area. The deposit is hosted within sheeted veins in the Dublin Gulch granodiorite and contact metamorphosed metasediments (Yusezyu Formation), and is characterised by enrichments in precious (Au, Ag), semi- (As, Te, Sb, Bi), and base metals (Mo, W, Pb, and Zn), with Au having a strong correlation with Bi ($r^2 = 0.9$) (Maloof et al, 2001).

3 Methodology

3.1 Sample selection and analytical techniques

Regionally metamorphosed Yusezyu Formation samples were obtained along the Dempster Highway, Silver Trail Highway, access road to Dublin Gulch, Canol Road, Nahanni Range Road, and from unmineralised sections of drillholes at the 3Aces orogenic gold occurrence (Fig. 1). Contact metamorphosed samples were taken from drillholes in the contact aureole surround the Dublin Gulch granodiorite (Fig. 1).

Mineralogical and textural associations in the samples (n 29) were examined under reflected and transmitted light, and under scanning electron microscope (SEM).

Laser ablation traverses were performed using a 100 µm beam moving at 100 µm/s relative to the sample at a repetition rate of 10 Hz and fluence of 2.5 J/cm^2. Traverses were conducted perpendicular to the major bedding/foliation. Laser ablation traverses were used to evaluate the distribution of elements of interest among mineral phases, to aid the identification of important metal-rich mineral phases.

Trace element compositions of pyrite (Py; n 180), pyrrhotite (Po; n 67), chalcopyrite (Ccp; n 18), chlorite (Cld; n 15), and biotite (Bt; n 7) were determined by LA-ICP-MS spot analyses from samples (n 29) distributed throughout the Selwyn basin area (Fig. 1). These *in situ* analyses were performed using a Resonetics Resolution laser ablation system equipped with a Coherent COMPex Pro 110 ArF Excimer laser, housed at CODES/Earth Sciences, University of Tasmania. The ArF excimer laser operates at a 193-nm wavelength with a 20-ns pulse width and was coupled to an Agilent 7700 quadrupole inductively coupled plasma mass spectrometer (ICP-MS). Quantitative LA-ICP-MS trace element analyses were performed following methods described by Gregory et al, (2015) for sulphide minerals, and methods described in Cave et al, (2016) for other minerals.

Whole rock and select trace element analyses were performed on regionally (n 31) and contact metamorophsed (n 9) samples by Actlabs and LabWest on XRF discs and pellets, and multiacid digestions finished with either ICP-OES or ICP-MS depending on the element. LOI was performed gravimetrically.

4 Results

4.1 Metal-rich mineral phases

Regionally metamorphosed samples: Laser ablation traverses completed on representative psammitic and pelitic samples, show irregular distributions of most trace elements, however some trends are recognised. Relatively high levels (counts per second; cps) of As, Sb, Te, Bi, Cu, Pb, and Zn predominately appear to correspond to relatively high levels in Fe and S. Reflected light microscopy shows these relatively high levels of As, Sb, Te, Bi, Cu, Pb, and Zn, as corresponding to the laser beam having passed through grains of pyrite. Zinc additionally appears as relative high levels at periods with corresponding relatively high levels of Mg, Al, Fe, and Si, with these corresponding to the laser beam having passed through chlorite lathes. Laser spot analyses show pyrite contains appreciable amounts of all these metals (Table 1), whereas chlorite contains significant amounts of Zn (Table 1).

	Unit	As ppm	Sb ppm	Bi ppm	Te ppm	Cu ppm	Pb ppm	Zn ppm
Py (n 180)	Min	<2.8	<0.19	<0.020	<0.082	<0.27	0.518	<0.35
	Max	11235	296	144	19.1	3521	3781	8537
	Median	612	22	3.5	1.5	237	216	21
Po (n 67)	Min	<1.4	<0.081	<0.020	<0.14	<0.84	<0.067	<0.48
	Max	37	7.3	18.8	5.8	5.3	53	4.4
	Median	<2.6	<0.20	0.67	<0.55	<2.2	0.57	<0.92
Ccp (n 11)	Min	<10.6	<0.37	<0.095	<0.92	340982	<0.40	475
	Max	<24	5.1	9.7	3.6	418599	16.9	822
	Median	<14.3	0.74	1.4	<1.3	360034	1.7	667
Cld (n 15)	Min	<5.8	<0.22	<0.074	<0.33	<2.3	<0.78	345
	Max	12.1	<0.79	0.322202	<6.0	22	7.3	952
	Median	<9.7	<0.66	<0.19	<2.3	<5.4	1.2	713
Bt (n 7)	Min	<8.5	<0.52	<0.02	<0.72	<3.7	<0.68	226
	Max	<13.3	<1.07	<0.29	<3.5	10.4	4.1	387
	Median	<9.3	<0.78	<0.16	<1.9	<4.9	0.88	335

Table 1. Minimum, Maximum, and median values for select mineral phases determined by LA-ICP-MS.

Contact metamorphosed samples: Laser ablation traverses completed on representative psammitic to pelitic biotite-bearing contact metamorphosed samples from Dublin Gulch, show extremely heterogeneous distributions of As, Sb, Te, Bi, Cu, Pb, and Zn. Distribution of these elements systematically vary with metamorphic textures, with these elements generally below detection in the quartz-albite segregations, whereas being detectable in the biotite ± mica segregations. In the quartz-albite and biotite ± mica metamorphic segregations large pyrrhotite grains with associated chalcopyrite are observed. When the laser beam passed over these grains relatively high levels (cps) of As, Sb, Te, Bi, Cu, Pb, and Zn are observed. However, *in situ* analyses shows these elements are significantly lower in pyrrhotite and chalcopyrite, relative to pyrite (from which it formed), except Cu and Zn in chalcopyrite (Table 1). Zinc is also present in relatively high levels (cps) at periods that corresponding with relatively high levels (cps) of Mg, K, Al, Fe, and Si, with SEM showing these as corresponding to the laser beam having passed through biotite lathes. Spot analyses performed on biotite show it contains significant amounts of zinc, however significantly less than chlorite (from which it formed) (Table 1).

4.2 Semi-metal, base metal, and volatile concentrations in whole rock

The Yusezyu Formation metasediments show heterogeneity in whole rock concentrations among individual samples, however, overall trends are recognised. Median values reveal regionally metamorphosed samples contain appreciable concentrations of As (28.4 ± 24.5 ppm), Bi (0.32 ± 0.26 ppm), Sb (3.4 ± 3.8 ppm), Te (0.09 ± 0.08 ppm), Pb (33.0 ± 24.3 ppm), and Zn (100.0 ± 29.2 ppm) that are all significantly higher than concentrations observed in the contact metamorphosed samples (As, 10.5 ± 7.7 ppm; Bi, 0.17 ± 0.12 ppm; Sb, 1.1 ± 2.2 ppm; Te, 0.03 ± 0.01 ppm; Pb, 11.2 ± 6.4 ppm; Zn, 65.1 ± 24.0 ppm). In contrast, Cu concentrations are observed being relative enriched, but more heterogenous in the contact metamorphosed samples (53.4 ± 31.6 ppm) relative to the regionally metamorphosed samples (42.2 ± 12.6 ppm). Sulphur median values are similar between the regionally metamorphosed samples (1.2 ± 1.2 wt %) and contact metamorphosed samples (1.1 ± 1.0 wt %).

Loss on ignition (LOI) values represent the loss of volatile phases (e.g., organics, H_2O, CO_2, and S) during high-temperature heating of the samples. These values are often used to show the potential of rocks to produce fluid (H_2O) during prograde metamorphism. Loss on ignition (LOI) values are significantly lower in the contact metamorphosed samples (2.1 ± 1.1 wt %) than in the regionally metamorphosed samples (5.9 ± 1.7 wt %). We suggest this indicates a significant proportion was lost as H_2O.

5 Discussion and conclusion

Mineral reactions are crucial in explaining the mobility of trace elements in metasediments during prograde metamorphism. In the regionally metamorphosed Yusezyu Formation samples, pyrite and chlorite are the most important host phases for semi- (As, Sb, Te, and Bi) and base metals (Cu, Pb, and Zn). Through prograde metamorphism these are converted to pyrrhotite and chalcopyrite, and biotite, respectively. These minerals contain significantly lower concentrations of semi- and base metals relative to the minerals from which they formed from (except for Cu and Zn in chalcopyrite), suggesting these mineral reactions make these metals available for mobilisation.

Whole rock concentrations show that relative to the contact metamorphosed samples, the regionally metamorphosed samples contain significantly higher concentrations of As, Sb, Te, Bi, Pb, and Zn (Fig. 2), and slightly higher concentrations of S (Fig. 2). Whereas Cu appears to be enriched (Fig. 2). Leaching of elements by concurrently produced metamorphic fluids, can efficiently mobilise elements from metasedimentary rocks during prograde metamorphism (e.g., Pitcairn et al., 2006, 2010; Hammerli et al. 2016). We suggest the significantly lower LOI values in the contact metamorphic samples (Fig. 2) reflects significant metamorphic fluid production that likely leached elements made available through mineral recrystallisation reactions.

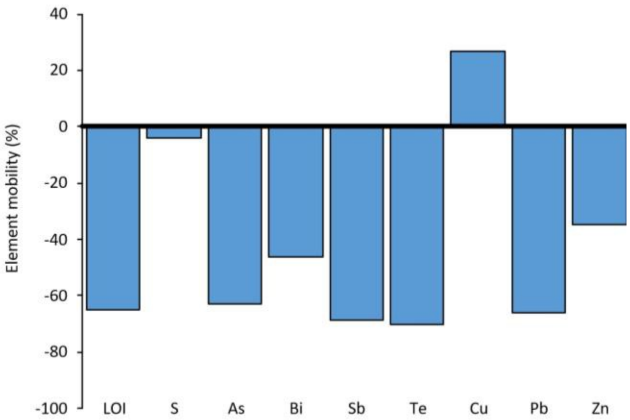

Figure 2. Element mobility diagram, showing percentage loss or gain of selected trace elements and the volatiles.

Mobilisation of this suite of elements could provide an alternative or additional metal source for RIRGS. Furthermore, the early assimilation of regionally metamorphosed sediments or later assimilation of contact metamorphosed sediments, could provide metals to the RIRGS. However, the assimilation of regionally metamorphosed metasedimentary rocks could provide significantly greater amounts of metals that are observed enriched in these deposits. Further work is required to: (1) Understand whether the metal-rich metamorphic fluid produced in the contact aureole interacted with the causative magma and was an important metal source for the RIRGS; (2) Investigate whether the assimilated metal-rich metasediments were an important metal source for the RIRGS.

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