The use of lithogeochemistry in delineating hydrothermal fluid pathways and vectoring gold mineralization in the Malartic district, Québec”

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Abstract

The Canadian Malartic world-class low grade, large tonnage gold deposit is located in the southeastern Superior Province of Canada. With reserves estimated at 6.38 Moz Au grading 1.10 g/t Au, it is currently the largest open pit mine in the Abitibi gold camp. The deposit is hosted predominantly by Pontiac Group metasedimentary rocks, Piché Group metavolcanic rocks, and quartz monzodiorite porphyritic intrusions. Stockwork-disseminated gold mineralization generally consists of a low-grade envelope of disseminated pyritic ore (0.35 to 1 g/t Au) grading inwards into higher grade (>1 g/t Au) stockwork and breccia zones. Hydrothermal alteration in the metasedimentary rocks displays a consistent zonation with distance from the main fluid pathways. Proximal alteration is characterized by a microcline±albite-quartz replacement-type assemblage, with lesser phlogopite, calcite±Fe-dolomite, pyrite and rutile. The distal alteration assemblage is dominated by biotite, microcline±albite, phengite, quartz, calcite, pyrite and rutile.

In this study, a lithogeochemical approach is used to assess the magnitude and distribution of fluid-rock interaction in the metasedimentary rocks of the Malartic district. The metaturbidites are separated into four sub-lithologies according to grain size characteristics to reduce the effects of primary depositional processes on mass change calculations. Despite the variability in protolith compositions, the metasedimentary rocks define a geochemically consistent, cogenetic sequence. The results of the mass transfer calculations indicate progressive gains in C-S-K₂O and LOI, as well as Au-Te-W-Ag±(As-Be-Sb-Bi-Mo-Pb) from background, through distal to proximal alteration zones (relative to least altered samples). Molar element ratio analysis (alkali/aluminium) indicates an increase in alkali metasomatism (K and Na) adjacent to the fluid pathways, which is manifested by the progressive stabilization of microcline and albite (at the expense of biotite and white mica).

Ore-associated pathfinder elements delineate broad enrichment patterns around the deposit, and can be used to outline hydrothermal fluid circulations in the Malartic district. A statistical approach based on the comparison of the mass balance results with the background composition provides robust constraints on the magnitude and extent of the lithogeochemical haloes. Most alteration envelopes extend along the S₂ fabric, and the largest lithogeochemical anomalies (*e.g.*, Au, W, Te and Ag) reach up to 10 kilometers in length, and 2 kilometers in width. These observations demonstrate that whole-rock lithogeochemistry provides a valuable vectoring tool toward gold mineralization in a regional exploration context.

1. Introduction

Major gold deposits in metamorphic terranes are typically surrounded by extensive wall-rock alteration haloes manifested by systematic changes in mineralogy away from the hydrothermal fluid pathways (Clark et al., 1989; Eilu and Mikucki, 1998; Bierlein et al., 1998; Eilu et al., 1999; Bierlein et al., 2000; Knight et al., 2000; Eilu and Groves, 2001; Goldfarb et al., 2005). The lateral zonation of alteration reflects the progressive decrease in fluid-rock interaction with increasing distance (*i.e.*, rock-buffering) from the hydrothermal centers (Khorzinskii, 1968; McCuaig et al., 1993; Ridley et al., 1996). Because the variations in alteration mineralogy are generally commensurate with mass transfer processes, lithogeochemical data can be used to assess the magnitude and spatial distribution of fluid-rock interaction (Bierlein et al., 1998; Eilu et al., 2001; Warren et al., 2007; Whitbread and Moore, 2004; Prendergast, 2007). In particular, methods involving mass balance calculations constitute a quantitative approach to evaluate the effects of metasomatic processes (Gresens, 1967; Grant, 1986; MacLean and Barrett, 1993; Mathieu, 2018). Likewise, molar element ratio analysis can be used to investigate mass transfer processes, and also offers a direct means to interpret alteration-related mineralogical reactions (Madeisky and Stanley, 1993; Warren et al., 2007; Stanley, 2017). The results of mass transfer calculations and molar element ratio analysis therefore provide key parameters for mapping the spatial distribution of alteration that defines the footprint of major gold deposits (Eilu and Mikucki, 1998; Eilu et al., 1999; Whitbread and Moore, 2004; Warren et al., 2007; Stock, 2012). Most notably, ore-related ‘pathfinder’ elements (*e.g.*, W, Te, Sb, Bi or As) can delineate lithogeochemical anomalies that extend far beyond the limits of the macroscopic hydrothermal alteration (Eilu and Groves, 2001; Whitbread and Moore, 2004; Perrouy et al., 2018).

In this study, we characterize the lithogeochemical signature of hydrothermal alteration at the Canadian Malartic stockwork-disseminated gold deposit (Québec), and extract parameters to map the intensity and distribution of fluid-rock interaction. This approach should prove especially useful in a mineral exploration context by providing potential lithogeochemical vectors toward gold mineralization (Warren et al., 2007; Stock, 2012; Halley et al., 2015). For this purpose, mass transfer calculations are conducted to evaluate the magnitude of the metasomatic processes and their spatial distribution across the Malartic district. In addition, molar element ratios are used to assess the mineralogical controls on alkali mobility.

2. Regional Geology

The Abitibi greenstone belt of Québec, in the southeast Superior Province, comprises world-renowned mining localities such as the Val d'Or, Malartic and Rouyn-Noranda gold districts (Fig. 1). Major gold deposits occur principally along a crustal-scale structure, the Cadillac-Larder Lake Fault Zone, which separates the Abitibi greenstone belt to the north from the Pontiac metasedimentary belt to the south. The former consists of a succession of mafic-ultramafic to felsic volcanic rocks of tholeiitic to calc-alkaline affinity (emplaced from 2750 to 2696 Ma; Ayer et al., 2002; Thurston et al., 2008), which was succeeded by greywacke-mudstone sedimentation between 2690 and 2685 Ma (Ayer et al., 2005; Frieman et al., 2017). South of the Cadillac-Larder Lake Fault Zone, the Pontiac Group consists of a turbidite sequence dominated by greywacke-mudstone that were deposited from 2685 to 2682 Ma (Davis, 2002). The Timiskaming Group metasedimentary rocks (alluvial-fluvial facies) were unconformably deposited on older units from 2677 to 2670 Ma (Ayer et al., 2005; Thurston et al., 2008). Several episodes of intrusive magmatism, the onset of which was contemporaneous with early volcanism, continued during to shortly after major tectonic activity (Sutcliffe et al., 1993; Davis et al., 2000; Chown et al., 2002). These intrusions range in composition from sodic tonalite-granodiorite (syn-volcanic), through calc-alkaline tonalite and alkaline syenite (syn-tectonic), to S-type two-mica granite and pegmatite (post-tectonic) (see Gaillard et al. 2018 for further details).

Regional deformation was polyphase, and comprised three main contractional events (Ayer et al., 2002; Robert et al., 2005; Perrouy et al., 2017). The first shortening episode (D_1) initiated immediately after the deposition of the turbidite-dominated basins, and was dominated by a fold-and-thrust style of deformation (Wilkinson et al., 1999; Bleeker, 2015). The second episode of deformation (D_2) followed deposition of the Timiskaming-type sedimentary rocks, and was manifested by north-south compression and local strike-slip transpression (Daigneault et al., 2002; Robert et al., 2005). This event was broadly contemporaneous with regional metamorphism (M_2), which ranged in grade from prehnite-pumpellyite to mid-amphibolite facies (Powell et al., 1995). Peak metamorphism was likely reached between 2665 and 2655 Ma, and postdated most D_2 deformation (Wilkinson et al., 1999; Ayer et al., 2005; Piette-Lauzière et al., 2018). The third episode of deformation (D_3) was characterized by dextral transcurrent motion along major fault zones (Daigneault et al., 2002; Ayer et al., 2005).

3. Local Geology

3.1. Host lithologies

The Canadian Malartic deposit is hosted by three lithotypes, namely the Pontiac Group metasedimentary rocks, the Piché Group metavolcanic rocks, and porphyritic quartz monzodiorite to granodiorite that intrude these units (Trudel and Sauvé, 1992). The Pontiac Group metasedimentary belt, at the northern margin of the Pontiac subprovince, forms a laterally extensive unit that stretches along the Cadillac-Larder Lake Fault Zone (Camiré et al., 1993; Mortensen and Card, 1993). It is composed of greywacke-mudstone successions, the petrographic and lithogeochemical characteristics of which will be described in detail later in this paper (see sections 6.1 and 6.2). The Piché Group (>2709 Ma; Pilote et al., 2015) forms a thin unit (<2 km) restricted to the Cadillac-Larder Lake Fault Zone, and consists dominantly of mafic-intermediate to ultramafic metavolcanic rocks, as well as minor mafic to felsic intrusions and metasedimentary rocks (Simard et al., 2013; Bedeaux et al., 2018). In the Malartic district, these units are intruded by a series of quartz monzodiorite to granodiorite porphyritic intrusions that were emplaced at 2677-2679 Ma (Helt et al., 2014; De Souza et al., 2015, 2016).

3.2. Deformation and metamorphism

The Malartic district was affected by a complex sequence of deformation and metamorphic events (Camiré and Burg, 1993; Benn et al., 1994; Ghassemi, 1996; Perrouty et al., 2017; Gaillard et al., 2018; Piette-Lauzière et al., 2018). The first episode of compressional deformation (D_1) was manifested by isoclinal folding of the Pontiac Group metaturbidites (F_1), and is generally recognized from inversions in the polarity of the sedimentary bedding (Perrouty et al., 2017; Gaillard et al., 2018). The second episode of deformation (D_2) produced moderately tight, upright folds (F_2) associated with a penetrative axial-planar cleavage (S_2) (Trudel and Sauvé, 1992). The S_2 foliation represents the dominant tectono-metamorphic fabric in the Malartic district (associated with M_2 metamorphism), and is defined by biotite±white mica and subordinate chlorite, as well as aligned aggregates of pyrite±pyrrhotite-chalcopyrite (Gaillard et al., 2018). A third episode of deformation (D_3) is represented by rare chevron folds (F_3) and small-scale kink bands, and is locally associated with late chlorite-calcite stringers (Desrochers, 1996; Perrouty et al., 2017).

The M_2 metamorphic event is reflected in the Malartic district by a gradual increase in grade from upper greenschist facies (biotite zone) adjacent to the Cadillac-Larder Lake Fault Zone to mid-amphibolite facies

(staurolite zone) a few kilometers (generally 1.5 to 2.5 kilometers) to the south (Fig.2). The axial-planar setting of the metamorphic foliation (S_2) relative to the F_2 folds suggests that prograde metamorphism (M_2) was broadly coeval with D_2 deformation (Gaillard et al., 2018). In addition, linear inclusion trails oriented parallel to the S_2 foliation in garnet and staurolite are interpreted to reflect a late-kinematic timing for peak metamorphism (M_2) relative to D_2 deformation (Piette-Lauzière, 2017; Gaillard et al., 2018). These textural interpretations are consistent with geochronological evidence from Lu-Hf dating on garnet, which indicate that peak metamorphism occurred at 2657.5 ± 4.4 Ma (Piette-Lauzière et al., 2018).

4. Canadian Malartic Gold Deposit

The Canadian Malartic deposit is a world-class low grade, large tonnage gold deposit that contains reserves estimated at 6.38 Moz Au at a grade of 1.10 g/t Au. The deposit overall gold endowment, calculated from the present and past production, plus mineral reserves and resources (excluding inferred) is estimated at 16.3 Moz Au (see Gaillard et al., 2018 and references therein). With an annual gold production of 0.63 Moz Au in 2017, the Canadian Malartic open-pit mine is currently the largest gold-producing operation in Canada.

4.1. Nature and distribution of mineralized zones

The Canadian Malartic stockwork-disseminated gold deposit consists of a low-grade (0.35 to 1 g/t Au) semi-continuous halo of pyritic alteration, which generally transitions inwards to higher grade (>1 g/t Au) stockwork and breccia zones (Fig. 3; Robert and Poulsen, 1997). The distribution of the mineralized zones is controlled by three main structures, which are interpreted to have acted as preferential pathways for hydrothermal fluids (Fig. 3). First, the Sladen Fault is a 3 km-long, E-W-trending, S-dipping ductile-brittle shear zone, and represents a first-order splay off the Cadillac-Larder Lake Fault Zone (Fig. 3; Trudel and Sauvé, 1992; De Souza et al., 2016). Second, the NW-SE deformation zones represent a series of parallel, high-strain bands axial-planar to F_2 folds (Fig. 3; Sansfaçon and Hubert, 1990; De Souza et al., 2016). Third, the Barnat Fault forms of a corridor of anastomosing shears that extend along the southern margin of the Cadillac-Larder Lake Fault Zone, parallel to the NW-SE deformation zones (Fig. 3; Trudel and Sauvé, 1992). Gold mineralization also displays a close spatial association with quartz monzodiorite to granodiorite porphyritic intrusions, most notably along faulted contacts with the metasedimentary and metavolcanic host rocks (Fig. 3; Helt et al., 2014; Perrouy et al., 2017).

4.2. Hydrothermal alteration

The Canadian Malartic deposit is typified by stockworks of quartz-biotite-carbonate-microcline±pyrite veinlets (v2) associated with a pervasive microcline-albite-biotite±(white mica)-carbonate-pyrite alteration (Robert, 2001; de Souza et al., 2015, 2016; Gaillard et al., 2018). Systematic variations in alteration reflect a lateral zonation of hydrothermal features away from the fluid corridors (de Souza et al., 2016; Gaillard et al., 2018). The proximal alteration is typified by a beige-brown replacement-type assemblage dominated by microcline±albite-quartz, with variable proportions of phlogopite, calcite, Fe-dolomite, pyrite and rutile (Fig. 5A-B). This alteration displays a strong genetic association with ore-stage (v2) veinlets, and coincides spatially with dense veining in stockwork and breccia zones (Fig. 5A-B).

In the metasedimentary rocks, the proximal alteration transitions outwards to a blue-grey distal alteration assemblage consisting of biotite, microcline±albite, phengite, quartz, calcite, pyrite and rutile (Fig. 5C-D). The strength of the distal alteration is controlled mainly by ore-stage (v2) veinlets, as manifested by a broad correlation of pyrite and calcite alterations with veining (v2) intensity (Fig. 5C-D). The transition from proximal to distal alteration is accompanied by a gradual increase in the proportions of biotite (Mg-rich) and white mica (phengite) at the expense of microcline±albite (Fig. 5C-D). The mineralogy of the distal assemblage is affected by the composition of the metasedimentary rocks, as indicated by increased phengite alteration in fine-grained mudstone beds (de Souza et al., 2016; Gaillard et al., 2018; Lypaczewski et al., in review) (Fig. 5C).

In addition, hydrothermal alteration is also manifested by a broad sulfidation-oxidation halo surrounding the main fluid pathways (Gaillard et al., 2018). This halo is delineated by systematic outward transitions in Fe-sulfide (from pyrite to pyrite±pyrrhotite) and Fe-Ti oxide (from rutile to ilmenite) minerals, and typically extends a few meters beyond the limit of the ore-shell (>0.35 g/t Au). These transitions are interpreted to reflect decreases in sulfidation (ΣaS) and oxidation (fO_2) parameters away from the hydrothermal corridors (Nesbitt, 1986a,b; Gaillard et al., 2018).

4.3. Ore mineralogy

Gold mineralization at Canadian Malartic consists of native gold and Au-(Ag)-bearing telluride minerals in quartz-biotite-carbonate-microcline±pyrite (v2) veinlets and associated alteration envelopes (Helt et al., 2014; De Souza et al., 2016; Gaillard et al., 2018). The ore assemblage is typified by native gold, petzite (Ag_3AuTe_2) and calaverite ($AuTe_2$), along with hessite (Ag_2Te), altaite ($PbTe$) and minor Bi-bearing

tellurides (Helt et al., 2014). These minerals are generally accompanied by minor chalcopyrite and galena, as well as rare sphalerite and molybdenite. Mineralogical and textural observations indicate a consistent association of native gold and telluride minerals with disseminated pyrite (Helt et al., 2014; Gaillard et al., in review). This association is generally manifested by the precipitation of gold-bearing minerals in the vicinity, or in direct contact with pyrite grains. Hydrothermal pyrite typically displays composite textures manifested by three main paragenetic stages (Type 1 to 3), the first and second of which are interpreted to have precipitated from ore-forming fluids (Gaillard et al., in review). Native gold and Au-(Ag)-telluride minerals also occur as small (sub-micron) inclusions and nano-particles in Type 1 and 2 pyrite, as indicated by elevated Au and ore-related element (Ag, Te, Pb and Bi) concentrations (Gao et al., 2015; Gaillard et al., in review).

5. Methods

5.1. Sampling strategy

A total of 596 metasedimentary rock samples were collected and analyzed for whole-rock major and trace element compositions (see Piercey et al. (2014) for details on the sampling protocol). The drill core and surface samples were taken from homogeneous intervals representative of the lithology and alteration at each site. Sampling was distributed across the Malartic district over an area of approximately 15×7.5 kilometers, thus providing a regional framework with which to assess the metasomatic effects associated with hydrothermal fluid-rock interaction (Fig. 2). Sampling density was increased near the deposit to assess the lithogeochemical signatures of the proximal and distal alteration facies. The regional distribution of samples was designed to characterize the background geochemical variations of the Pontiac Group metasedimentary rocks. With respect to the latter, samples were divided into three groups according to their alteration characteristics, from background samples (n=443) with no visible evidence of hydrothermal alteration, to distal (n=123) and proximal (n=30) alteration types.

5.2. Whole-rock lithogeochemical analyses

The samples were crushed, split and pulverized with mild steel to <75 µm (package Prep-31) by ALS Canada (Vancouver, BC). The major and minor element compositions were determined after lithium fusion using wavelength dispersive X-ray fluorescence analysis (package 4C-XRF Fusion) by Activation Laboratories (Ancaster, ON). The minor and trace element compositions, including those of rare earth

elements (REE), were analyzed using a combination of ICP-AES and -MS after sodium peroxide fusion (package GE ICM90A) by SGS Canada (Burnaby, BC). Whole-rock major, minor and trace element compositions, including gold concentrations, were also determined using ICP-AES and ICP-MS analysis following partial digestion using aqua regia (package ME-MS41L) by ALS Canada. Whole-rock sulfur and carbon analyses were carried out using a LECO analyzer (infrared absorption spectroscopy after combustion) by SGS Canada (package GE CSA06V). The accuracy and precision of the whole-rock lithogeochemical analyses were monitored through systematic incorporation of standard, blank and duplicate samples. Details of the quality control and assurance protocols (QA/QC), and cross-validation results are provided in [Perrouy et al. \(2018\)](#).

5.3. Evaluation and preparation of the lithogeochemical dataset

A systematic approach was implemented to evaluate the lithogeochemical dataset as a prerequisite for further investigation and statistical analysis. Elements with more than 5% of values below the lower detection limit (non-detect values) were discarded (left-censored datasets). In addition, elements with a large number of values close to detection limit (*i.e.*, more than 50% of analyses below 3×LOD value) were also removed. The presence of non-detect values is typically a source of complication for subsequent data analysis and calculation of summary statistics ([Helsel, 2005](#); [Huston and Juarez-Colunga, 2009](#)). Simple methods for handling censored values (deletion or arbitrary replacement) typically disregard the effects of closure that characterize compositional data ([Aitchison, 1986](#)) and have been shown to generate biased estimates of the mean and variance ([Helsel and Gilliom, 1986](#); [Makvandi et al., 2016](#)). In this study, a multivariate imputation method was implemented to replace the censored values using the `zCompositions` package in the R software environment ([Hron et al., 2010](#); [Palarea-Albaladejo and Martín-Fernández, 2013, 2015](#)). The imputation method relied on the robust isometric log-ratio expectation-maximisation algorithm, an iterative compositional procedure that estimates the non-detect values through the preservation of the multivariate relative covariation structure of the dataset ([Palarea-Albaladejo et al., 2014](#)).

5.4. Mass balance calculations

Mass transfer associated with hydrothermal alteration was calculated following the principles of [Gresens \(1967\)](#), wherein the evaluation of mass changes is based on the comparison of altered rock compositions with those of their least altered rock equivalents (precursors). In the absence of density measurements, the

overall mass/volume change caused by hydrothermal alteration was estimated using immobile element ratios (MacLean, 1990). Elements such as Al, Ti and Zr are generally considered to be immobile in hydrothermal systems under a wide range of physico-chemical conditions (Finlow-Bates and Stumpf, 1981; MacLean and Barrett, 1993). Because immobile element pairs retain constant ratios during alteration, the selection of immobile elements for mass change calculations can be assessed graphically from their linear relationships in bi-variate plots (MacLean and Kranidiotis, 1987). As shown by Warren et al. (2007), the use of immobile element ratios in place of density and volume factor terms yields a simplified expression of Gresens' mass change equation, which is equivalent to that of MacLean and Barrett (1993). This approach involves the calculation of the reconstructed composition of a component X, corrected for the overall mass/volume change produced by hydrothermal alteration:

$$RC_X^A = C_X^A \times (C_{imm.}^P / C_{imm.}^A) \quad (1)$$

where:

- RC_X^A is the reconstructed composition of a component X in sample A (altered rock)
- C_X^A is the concentration of a component X in A (altered rock)
- $C_{imm.}^P / C_{imm.}^A$ is the concentration ratio of an immobile component in P (precursor) to A (altered rock)

In this study, the mass changes are expressed relative to the composition of the precursor rock, and correspond to the ratio of the reconstructed composition of component X in the sample of interest to the concentration of the same component in the precursor rock:

$$\Delta_X = RC_X^A / C_X^P \quad (2)$$

where:

- Δ_X is the mass change of a component X, relative to the precursor composition
- C_X^P is the concentration of a component X in P (precursor)

The expression of the mass transfer as a ratio relative to the precursor composition yields results that are restricted to the positive number space, which facilitates data manipulation (*e.g.*, log-transformation) for subsequent statistical calculations and map representation (*cf.* Perrouy et al., 2018). In this context, the values below unity correspond to depletions, whereas values above unity represent enrichments relative to the least altered samples (*e.g.*, concentration factor).

5.5. Lithogeochemical mapping and spatial data analysis

The results of the mass change calculations are presented as a series of maps that illustrate the distribution of fluid-rock metasomatic interactions in the metasedimentary rocks of the Malartic district. Spatial interpolation between the discrete data points was conducted using a minimum curvature gridding algorithm in the Geosoft Oasis Montaj® software. The complete dataset used to produce the lithogeochemical maps is reported separately in the supplementary material attached to this study.

Because the selected criteria for the spatial representation of the mass changes remain partly arbitrary (e.g., the color scale), a statistical approach was implemented to investigate the magnitude and distribution of the metasomatic haloes. The aim of this method is to establish a statistical framework in order to compare the spatial extent of the different lithogeochemical anomalies, and thus to provide robust constraints on the mobility of the pathfinder elements. Our approach therefore consists in formulating the mass balance results in terms of standard deviation distance relative to the background population mean (standard score). This method is generally referred to as standardization and is most commonly applied to normally-distributed datasets. For most elements, however, the distribution of the mass change data in the background metasedimentary rock population (n=443) is best approximated by a log-normal distribution. For this reason, the geometric mean ($\bar{x}^*$) and multiplicative standard deviation (s^*) were used to characterize the central tendency and dispersion of the data, respectively (Limpert et al., 2001). Given a component X, these parameters are expressed as:

$$\bar{x}^* = \exp \left(\frac{1}{n} \cdot \sum_{i=1}^n \ln(x_i) \right) \quad (3)$$

$$s^* = \exp \left(\sqrt{\frac{1}{n-1} \cdot \sum_{i=1}^n \left[\ln \left(\frac{x_i}{\bar{x}^*} \right) \right]^2} \right) \quad (4)$$

where:

- n represents the number of observations
- x_i corresponds to the mass change values (Δx) calculated for a component X

Accordingly, the geochemical anomalies are evaluated relative to the background compositions using a standardization algorithm that is based upon the multiplicative properties of the log-normal distribution:

$$Z_{\Delta X}^* = \frac{\ln(x_i) - \ln(\bar{x}_{\text{background}}^*)}{\ln(s_{\text{background}}^*)} \quad (5)$$

where:

- $Z_{\Delta X}^*$ is the standardized mass change value for a component X relative to the background distribution
- x_i is the mass change values (Δx) calculated for a component X
- $\bar{x}_{\text{background}}^*$ represents the geometric mean of the background population
- $s_{\text{background}}^*$ represents the multiplicative standard deviation of the background population

Interpolated maps of the standardized mass change data were produced following the same guidelines as for the raw mass balance data. A unique color scale (class interval representation), based on multiples of the standard deviation distance to the mean value (log-transformed) was used for all the variables.

6. Pontiac Group Metasedimentary Host Rocks

6.1. Petrography of the background metaturbidites

The Pontiac Group metasedimentary rocks form a flyschoid sequence composed of interstratified beds of mudstone (pelitic) to greywacke (psammitic) (Dimroth et al., 1982; Mortensen and Card, 1993; Ghassemi, 1996). The planar-stratified sedimentary beds range in thickness from a few centimeters up to a meter, and generally display parallel, millimeter-scale internal laminations (Fig. 4a-b). Individual strata commonly display evidence of graded-bedding, as manifested by a progressive upward decrease in detrital grain size (Fig. 4a-b). The clastic particles range in diameter from <50 μm in mudstone, to 2 mm in greywacke, and reach a maximum of 12 mm in rare conglomeratic beds (Ghassemi, 1996). The vertical succession of the sedimentary facies is generally consistent with a partial Bouma sequence, which suggests that the Pontiac Group wackes were deposited from turbidity currents (Benn et al., 1994; Card and Poulsen, 1998). This interpretation is further supported by the presence of internal sedimentary structures typical of turbidites including load casts, cross-laminations and flame structures (Goulet, 1978; Ricci-Lucchi and Amorosi, 1978).

The mineralogy of the Pontiac Group metasedimentary rocks varies systematically as a function of the protolith grain size and metamorphic grade. Greenschist facies metaturbidites are composed of quartz, plagioclase and biotite, with lesser but variable proportions of white mica, chlorite, epidote, ilmenite, pyrite, pyrrhotite and magnetite (Fig. 4d-f). Because finer-grained turbidite layers originally contained a greater

amount of clay minerals, the mudstone facies generally displays higher modal proportions of white mica and biotite compared to the greywacke. Such modal variations are therefore interpreted to reflect changes in bulk-rock compositions caused by primary sedimentary processes (e.g., aluminous nature of pelitic layers). At higher metamorphic grades, variations in protolith composition partly determine the mineralogy of the peak metamorphic assemblage; more specifically, staurolite (and garnet) porphyroblasts form preferentially in fine-grained pelitic beds of the turbiditic sequence (Gaillard et al., 2018; Piette-Lauzière et al., 2018). The metamorphic index minerals therefore provide key indicators to discriminate among the sedimentary facies at higher metamorphic grade (i.e., amphibolite facies), wherein metamorphic recrystallization of quartz and plagioclase typically forms a granoblastic polygonal texture that obliterates the primary sedimentary textures (Ghassemi, 1996).

6.2. Lithogeochemistry of the background metaturbidites

The variations in protolith grain size are manifested by consistent changes in bulk-rock lithogeochemical compositions. Such variations are interpreted to reflect predominantly the effects of physical sorting (grain size and density) during transport and deposition of the clastic sediments (Fig. 4). Therefore, in order to evaluate the effects of the sedimentary processes on lithogeochemical variability (Cai et al., 2008; Mishra and Sen, 2011), the metasedimentary rocks were separated into four sub-lithologies according to textural (grain size) and mineralogical characteristics, namely, greywacke (n=247), siltstone (n=134) and mudstone (n=188), as well as a group defined by lower Σ REE concentrations (n=27) and a distinct chondrite-normalized REE profile. The variations in whole-rock major element concentrations among the sub-lithologies in the background metasedimentary rocks are illustrated in Figure 6 using box and whisker diagrams (additional plots for minor and trace elements are provided in Appendix 1).

The greywacke (coarse-grained) fraction of the metasedimentary rocks is generally characterized by higher concentrations of SiO₂ (average 66.1 wt.% in the background population) relative to the siltstone (65.0 wt%) and mudstone (60.9 wt%) fractions (Fig. 6). In addition, greywacke also displays elevated concentrations of Na₂O (3.73 wt%) and CaO (2.59 wt%) compared to siltstone (3.64 and 2.48 wt%, respectively) and mudstone (2.96 and 2.10 wt%, respectively) (Fig. 6). These variations are interpreted to reflect higher modal proportions of quartz and plagioclase in the coarse-grained sediments (Fig. 4). In contrast, the mudstone (fine-grained) fraction has higher average concentrations of Al₂O₃ (17.7 wt%) relative to siltstone (15.7 wt%) and greywacke (15.3 wt%). In addition, increases in the concentrations of

Fe₂O₃ (from 5.32 to 6.66 wt%), K₂O (from 2.09 to 3.27 wt%), MgO (from 2.77 to 3.45 wt%) and TiO₂ (from 0.54 to 0.67 wt%) are also associated with decreasing grain size, from greywacke to mudstone (Fig. 6). These trends are interpreted to be mainly controlled by increasing proportions of hydrous phyllosilicates (dominantly biotite and white mica) in the fine-grained sediment fractions, and likely correspond to elevated proportions of clays in the protolith (Camiré et al., 1993; Fig. 4). This interpretation is supported by a general increase in loss on ignition (LOI), from 1.25 wt% in greywacke, to 1.98 wt% in mudstone (Fig. 6). These trends also coincide with a progressive increase in the average concentrations of most minor elements (e.g., Ba, Cr, V, Rb, Ni, Co, Ga) with decreasing grain size, except for antithetic decreasing trends in Sr and Zr concentrations (Appendix 1). The minor element enrichments documented in the fine-grained fractions are interpreted to be controlled by greater proportions of phyllosilicates (biotite±white mica) and subordinate oxide phases (ilmenite±magnetite), whereas opposite trends (i.e., towards the greywacke fraction) are likely attributable to dilution by quartz and plagioclase (Cai et al., 2008; Mishra and Sen, 2011). The low Σ REE group of metasedimentary rocks has major (Fig. 6) and minor (Appendix 1) element compositions that are intermediate between those of siltstone and mudstone. However, the low Σ REE sediments are consistently depleted in REE (Fig. 7) and display lower abundances of Ni and Co compared to the other sub-lithologies (Appendix 1).

Despite the variability in protolith compositions inherent to primary sedimentary processes, the linear variations documented for Pontiac Group metaturbidites on immobile-immobile bivariate diagrams define a lithogeochemically consistent metasedimentary sequence (Helt et al. 2014). Specifically, the positive correlation between Al₂O₃ and TiO₂ ($r=0.78$) suggests a strong cogenetic relationship across the stratigraphic sequence (Fig. 7a). The geochemical signatures of the metaturbidites were further assessed by comparing REE patterns normalized to chondrite composition (Fig. 7b). Aside from a limited number of samples characterized by a distinct signature and a low total Σ REE content ($n=27$), the resulting profiles are nearly identical and differ mainly in the absolute REE concentrations ($n=569$). These similarities suggest that the Pontiac Group metaturbidites likely had a single provenance (Camiré et al., 1993), although the low Σ REE population may reflect intermittent (and minor) contribution of clastic material from a source (Fig. 7b).

7. Mass Transfer in Hydrothermally Altered Metasedimentary Rocks

The mass changes associated with hydrothermal alteration in the metasedimentary rocks characterize the lithogeochemical signature of the Canadian Malartic deposit, and can be used to develop parameters for mapping the intensity and distribution of fluid-rock interactions at the district scale. However, as noted above, the evaluation of mass transfer in sedimentary rocks is often hampered by geochemical variability in protolith compositions (Fig. 6; Appendix 1). To reduce the effects of such variations on the mass transfer calculations, the metasedimentary rocks were divided into four sub-lithologies according to grain size and REE signatures (Figs. 6-7). In the Malartic district, the background populations of the greywacke, siltstone, mudstone and low Σ REE sediments display relatively narrow compositional ranges (Fig. 6; Appendix 1). The primary variations in each sub-lithology are therefore interpreted to be negligible compared with those of the sedimentary sequence as a whole, thereby providing an appropriate rock classification to quantify alteration-related mass transfer.

7.1. Least altered samples

A set of least altered samples (n=20) was selected from the Pontiac Group metasedimentary host rocks based on petrographic (textural and mineralogical features) and lithogeochemical characteristics. Average least altered compositions were calculated separately for each of the sub-lithologies from representative samples of greywacke (n=6), siltstone (n=4), mudstone (n=6), and low Σ REE (n=4) metasedimentary rocks. The least altered samples were carefully inspected to avoid any signs of hydrothermal alteration or surficial weathering. Because gold mineralization is typically associated with disseminated pyrite and carbonate (calcite $\pm$ Fe-dolomite) alteration, the criteria for the selection of the least altered samples included low concentrations of Au (<5 ppb), S (<0.3 wt%) and C (<0.3 wt%). The distance to the ore shell was also taken into consideration, so that the least altered samples were derived from drill core and outcrops located >1.5 kilometers from to the Canadian Malartic deposit.

7.2. Immobile elements

The overall effects of mass/volume changes caused by hydrothermal alteration were evaluated by normalizing the compositions of the altered samples to those of their respective precursors using immobile element ratios (MacLean and Kranidiotis, 1987). Element immobility was tested using bi-variate plots, in which immobile elements define linear arrays that pass through the origin (MacLean, 1990). The bulk-rock

concentrations of Al_2O_3 and TiO_2 were shown to delineate the best linear trend ($r=0.78$; Fig. 7a), thereby indicating that these elements remained essentially immobile during alteration (MacLean and Barrett, 1993; Helt et al., 2014). For this reason, immobile element ratios calculated from Al_2O_3 concentrations were used to assess the mass transfer associated with alteration.

7.3. Mass transfer associated with hydrothermal alteration

Average mass changes were determined for proximal and distal alteration assemblages to evaluate the metasomatic effects associated with ore-forming processes, and to identify potential pathfinder elements that could be used as vectors to gold mineralization. The results are presented as a series of box and whisker diagrams in Figures 8-9 and Appendix 2 for the distal ($n=123$) and proximal ($n=30$) alteration zones, and are evaluated relative to the background metasedimentary rock population ($n=443$). Comparison of the average compositions of altered and least-altered rocks ($n=20$) indicates a significant increase in the concentrations of $\text{Au-Te-W-Ag}\pm(\text{As-Be-Sb-Bi-Mo-Pb})$ as well as $\text{C-S-K}_2\text{O}$ and LOI in the rocks associated with gold mineralization (Figs. 8-9).

The results of mass transfer calculations define systematic enrichments from background compositions, through distal to proximal alteration zones. The proximal and distal alteration assemblages are characterized by substantial gains in C (mean $\Delta_{\text{C}} = 56.2$ and 21.0 , respectively), S ($\Delta_{\text{S}} = 18.4$ and 4.8), K ($\Delta_{\text{K}_2\text{O}} = 2.6$ and 1.7) and LOI ($\Delta_{\text{LOI}} = 6.3$ and 3.0), compared to least-altered equivalents (Fig. 8). These observations are consistent with mineralogical characteristics of the alteration assemblages, and correlate with increasing modal proportions of $\text{calcite}\pm\text{Fe-dolomite}$ and pyrite with increasing proximity to the hydrothermal fluid pathways (Fig. 5; De Souza et al., 2016; Gaillard et al., 2018). Potassium addition in hydrothermally-altered rocks is interpreted to reflect the effects of microcline and $\text{biotite}\pm\text{white mica}$ alteration (Fig. 5; Helt et al., 2014; Gaillard et al., 2018). Small, but significant gains in Na ($\Delta_{\text{Na}_2\text{O}} = 1.37$ and 1.06 in proximal and distal alteration zones, respectively) and Ca ($\Delta_{\text{CaO}} = 1.48$ and 1.13) are restricted mainly to the proximal alteration assemblage, and are associated with pervasive feldspathization ($\text{microcline}\pm\text{albite}$) and carbonate alteration (Fig. 8). Other major elements, including Si ($\Delta_{\text{SiO}_2} = 0.99$ in altered rocks), Mg ($\Delta_{\text{MgO}} = 1.06$), Ti ($\Delta_{\text{TiO}_2} = 1.09$) and Fe ($\Delta_{\text{Fe}_2\text{O}_3} = 1.11$) display only limited mass changes related to fluid-rock interaction, and are relatively constant in the different alteration zones (Appendix 2).

Gold mineralization in the proximal and distal alteration zones is associated with major gains in Au (Δ_{Au} of 1968 and 586 , respectively), along with substantial enrichments in Te (Δ_{Te} of 146.2 and 21.5),

W (Δ_W of 65.8 and 17.1), Ag (Δ_{Ag} of 41.7 and 6.8), As (Δ_{As} of 16.8 and 13.8), Be (Δ_{Be} of 8.4 and 3.8), Sb (Δ_{Sb} of 5.3 and 3.3), Bi (Δ_{Bi} of 7.4 and 2.3), Mo (Δ_{Mo} of 13.8 and 2.2) and Pb (Δ_{Pb} of 6.3 and 2.5) relative to least-altered equivalents (Fig. 9). These enrichments are consistent with the mineralogy of the ore assemblage, and thus define the metallic signature of the deposit (Helt et al., 2014; Gaillard et al., 2015; De Souza et al., 2015, 2016). Substantial mass gains documented for Au, Te, Ag, Pb and Bi in the mineralized samples reflect the presence of native gold and Au-Ag-(Pb-Bi)-bearing telluride minerals such as petzite, hessite, altaite and calaverite (Gaillard et al., in review). By contrast, bulk-rock enrichments in W and Sb in the altered rocks are attributed predominantly to the precipitation of rutile, which tends to be anomalous in these elements at Canadian Malartic (Clark et al., in prep.).

7.4. Correlation relationships among mass change values

The mineralogical controls on the metasomatic processes associated with ore-forming processes were evaluated from the correlation relationships among mass change values (Fig. 10). Given the relative nature of the mass transfer calculations (*i.e.*, normalization to a precursor composition), such correlations are essentially unaffected by the effects of closure that generally affect compositional data (Aitchison, 1986). In addition, these correlation relationships are less influenced by primary depositional features compared to raw lithogeochemical data, and thus provide insights into the mechanisms that govern metasomatic reactions and metal distribution (Libbey and Williams-Jones, 2016).

The linear correlation ($r=0.66$) between Δ_{Au} and Δ_S mass changes reflects a close spatial and genetic relationship between gold mineralization and sulfide minerals (Fig. 10). Gold mass change values (Δ_{Au}) also correlate positively with Δ_{Te} (0.66) and Δ_{Ag} (0.62), thus suggesting similar modes of transport and precipitation for Au, Ag and Te (Fig. 10). These interpretations are further supported by petrographic observations, most notably by the association of native gold and (Au $\pm$ Ag)-telluride minerals in inclusions and fracture-fillings in hydrothermal pyrite (Gaillard et al., in review). For these reasons, gold deposition has been interpreted to result from the destabilization of gold-bisulfide complexes in response to wall-rock sulfidation (Helt et al., 2014). In addition, gold mass change values correlate positively with those of other associated metals, including Δ_W (0.66), Δ_{Be} (0.58) and Δ_{Bi} (0.48) (Fig. 10). Because the enrichment factors calculated for such trace elements are log-normally distributed, the correlation relationships among these variables are however best characterized from log-transformed values (Appendix 2). Most significantly, the correlation relationships among log-transformed values define a strong association for Δ_{Au} with Δ_{Ag} (0.82),

Δ_{Te} (0.80), Δ_{W} (0.78), Δ_{Be} (0.70), Δ_{As} (0.54), Δ_{Bi} (0.53) and Δ_{Pb} (0.50). Consequently, as discussed below, these metals are likely to have utility as pathfinder elements to identify areas affected by alteration, and to delineate vectors toward ore zones in the Malartic district (cf. Eilu and Mikucki, 1998; Eilu et al., 2001).

Because major element data reflect the primary rock-forming minerals in the host metasedimentary rocks, mass transfer associated with hydrothermal alteration for these components typically defines lower magnitude changes compared to the trace elements. For this reason, the correlation coefficients for major element mass changes are generally lower than those of the pathfinder metals (Fig. 10). Nonetheless, major element mass changes directly reflect the effects of fluid-rock interaction on alteration mineralogy, and thus provide important information with which to evaluate the magnitude of metasomatic reactions adjacent to hydrothermal fluid pathways (Eilu and Groves, 2001; Whitbread and Moore, 2004). The data indicate that there is a strong colinear relationship between Δ_{LOI} and Δ_{C} mass changes ($r=0.84$), as well as weaker positive correlations between Δ_{CaO} and Δ_{C} ($r=0.51$) and Δ_{CaO} and Δ_{LOI} ($r=0.40$); these are interpreted to be the result of carbonate alteration (Fig. 10). High correlation coefficients between Δ_{LOI} and Δ_{S} ($r=0.75$), and between Δ_{C} and Δ_{S} ($r=0.64$) further indicate a strong coupling of carbonate (calcite $\pm$ Fe-dolomite) and sulfide (pyrite) alteration. Host-rock sulfidation was also accompanied by pervasive alkali metasomatism (K_2O and Na_2O), as demonstrated by a strong positive correlation relationship between $\Delta_{\text{K+Na}}$ and Δ_{S} mass changes ($r=0.72$). The above notwithstanding, Δ_{K} displays a weak negative correlation with Δ_{Na} ($r=-0.29$), which suggests complex mineralogical and physico-chemical controls on potassic-sodic alteration in zones of pervasive microcline $\pm$ albite replacement (Mathieu, 2018; see below).

8. Molar Element Ratios

The mineralogical reactions that controlled the mass transfer processes during hydrothermal fluid-rock interaction were evaluated using molar element ratios (Madeisky and Stanley, 1993; Eilu and Groves, 2001; Whitbread and Moore, 2004; Prendergast, 2007; Stanley, 2017). This approach is particularly well-suited to the analysis of metasomatic processes, as molar proportions provide a direct means to correlate changes in bulk-rock lithogeochemistry to alteration mineralogy (Madeisky and Stanley, 1993; Warren et al., 2007). Because they are expressed relative to a conserved component, Pearce element ratios are not affected by closure, and can be used to quantify the lithogeochemical and mineralogical variations associated with hydrothermal alteration (Pearce, 1968; Madeisky and Stanley, 1993). Binary plots based on alkali/aluminium molar ratios (Na/Al vs. K/Al) are presented in Figure 11, and illustrate the mineralogical

controls on alkali mobility in metasedimentary rocks of the Malartic district (Davies and Whitehead, 2006). Specific nodes in such binary plots represent stoichiometric proportions of common alteration minerals, including feldspars (microcline, albite and plagioclase) and phyllosilicates (biotite, muscovite and chlorite) (Fig. 11; Madeisky and Stanley, 1993; Warren et al., 2007). However, molar element ratio binary plots only capture a partial representation of the system complexity, thereby limiting the evaluation of mass transfer processes to the projected mineral phases.

Two versions of the same molar element ratio binary plot (Na/Al vs. K/Al) are presented in Figure 11. In the first, the metasedimentary rocks are color-coded based on petrographical characteristics (grain size) to illustrate the effects of depositional processes on whole-rock composition (Fig. 11A). Most background metasedimentary rocks at Malartic fall within the field outlined by the minerals typical of the metamorphic assemblage, namely biotite, white mica and plagioclase (Fig. 11A). Increasing grain size from mudstone to greywacke shows a general trend toward higher Na/Al and lower K/Al values (Fig. 11A). These variations are interpreted to reflect progressive mineralogical changes with increasing grain size, as manifested by a trend toward the plagioclase stoichiometric node (*i.e.*, away from biotite and white mica) (Fig. 11A). These results suggest that variations in protolith composition caused by the primary sedimentary processes exert a strong control on the mineralogy of the background metamorphic assemblage.

Metasomatic effects associated with ore-forming processes were evaluated by dividing metasedimentary rocks according to hydrothermal alteration characteristics (Fig. 11B). Mass transfer processes in altered rocks are manifested by a general increase in K/Al and/or Na/Al ratios relative to background compositions. These variations delineate a broad gradient from background through distal to proximal alteration facies, which is interpreted to reflect progressive changes in mineralogy (and mineral chemistry) in response to increasing alteration intensity (Fig. 11B). The metasedimentary rocks that underwent distal alteration typically fall within a field delimited by biotite, white mica and albite, and partially overlap background compositions. By contrast, the metasedimentary rocks from the proximal alteration zone are characterized by elevated K/Al ratios, and fall within a narrow compositional field bounded by biotite, microcline and albite (Fig. 11B). These results suggest that increasing alkali (K-Na) metasomatism from distal to proximal alteration zones was controlled by the increasing stabilities of microcline and albite (at the expense of biotite and white mica), in agreement with petrographic observations. Molar element ratios therefore provide a

powerful means with which to evaluate the distribution of alteration minerals in the footprint of major hydrothermal systems.

9. Spatial Distribution of Hydrothermal Fluid-Rock Interactions

The results of mass transfer calculations were used to assess the magnitude and spatial distribution of metasomatic processes in the metasedimentary rocks of the Malartic district. A compilation of geochemical maps is presented in **Figure 12** to illustrate the distribution of mass changes for selected major (alkali and volatile) and pathfinder components. For this purpose, the mass transfer data for each component were first transformed using a Z-score standardization algorithm ($Z_{\Delta X}^*$), and expressed in units of multiplicative standard deviation (s^*) relative to the geometric mean ($\bar{x}^*$) of the background distribution (see **section 5.5**). This approach facilitates the direct comparison of the metasomatic haloes (spatial extent and magnitude).

The spatial distribution of the gold mass changes (Δ_{Au}) delineates a broad envelope of elevated values centered on the Canadian Malartic deposit (**Fig. 12A**). As expected, the strongest gold enrichment occurs in the deposit area, and generally corresponds to values exceeding the background average composition by more than two multiplicative standard deviations (*i.e.*, $Z_{\Delta Au}^* > 2$) (**Fig. 12A**). Specifically, samples collected from the open-pit ($n=170$) have an average $Z_{\Delta Au}^*$ value of 3.2, which corresponds to an average enrichment factor (Δ_{Au}) of 690 relative to the least-altered samples. The distribution of high $Z_{\Delta Au}^*$ values (*i.e.*, $Z_{\Delta Au}^* > 1$) extends beyond the limits of the deposit and defines a semi-continuous halo oriented parallel to the S_2 foliation. Significantly, the anomalous areas defined by Au mass gains include, in addition to the deposit itself, the main hydrothermal centers and prospects in the district, including the Cartier, Radium, Alpha and Bravo zones (**Fig. 12A**).

The geochemical anomalies defined by pathfinder trace elements associated with gold mineralization are shown in **Figure 12 B to G**. Notably, the spatial distributions of mass change values for Te, W, and Ag delineate district-scale alteration footprints around the Canadian Malartic deposit (**Fig. 12B-D**). The mass gains calculated for these elements are typically the highest within the open-pit area, and decrease with distance away from the deposit (**Fig. 12B-D**). The Te, W and Ag anomalies contrast markedly with the background compositions; samples from the open-pit ($n=170$) display pronounced mass gains compared to background metasedimentary rocks, with average $Z_{\Delta Te}^*$, $Z_{\Delta W}^*$ and $Z_{\Delta Ag}^*$ values reaching 2.9, 2.3 and 2.7, respectively (**Fig. 12B-D**). Such levels correspond to average Δ_{Te} , Δ_W and Δ_{Ag} enrichment factors of 35.8,

23.4 and 10.6, respectively. The mass gain patterns for these elements define semi-continuous alteration envelopes surrounding the deposit, and extend along strike for >10 kilometers (Fig. 12B-D). The geochemical anomalies delineated by Te, W and Ag correspond closely to the dispersion halo outlined by the gold mass gains. Because it is not affected by false positive anomalies related to outliers, W (and to a lesser extent Ag) displays the most consistent pathfinder footprint across the district (Fig. 12B-D).

The distributions of mass change values for As (Δ_{As}), Be (Δ_{Be}), Sb (Δ_{Sb}) and Pb (Δ_{Pb}) also define anomalies related to gold mineralization (Fig. 12E-H). Arsenic and Sb display moderate enrichments in the immediate deposit area compared to the least-altered equivalents, and correspond to average $Z_{\Delta As}^*$ and $Z_{\Delta Sb}^*$ values of 0.9 and 0.8, respectively (n=170). These elements delineate anomalies that extend towards the southeast in the direction of the Bravo zone ($Z_{\Delta As}^*$ and $Z_{\Delta Sb}^* > 1$) (Fig. 12E,G). The distribution of Be mass change values (Δ_{Be}) outlines a geochemical zoning with respect to the deposit, which is however partially masked by a number of false anomalies to the south and west of the district (Fig. 12F). Although the highest Pb enrichment factors (Δ_{Pb}) occur within, and adjacent to the deposit, the distribution of Pb mass change values is relatively erratic across the district (Fig. 12H).

The spatial distribution of mass change values for mobile alkali and volatile components such as C, S, K₂O and LOI is presented in Figure 12 I-L. Significantly, C and S display strong enrichments in the deposit area, as shown by average $Z_{\Delta C}^*$ and $Z_{\Delta S}^*$ open-pit values of 1.6 and 1.4, respectively (n=170). These mass gains also delineate a broad S₂-parallel halo beyond the deposit, which is characterized by local enrichments ($Z_{\Delta C}^*$ and $Z_{\Delta S}^* > 1$) that coincide with the locations of other gold prospects in the district (e.g., the Cartier, Radium, Alpha and Bravo zones) (Fig. 12I-J). The distribution of K₂O mass change values delineates a lithogeochemical anomaly that is mainly restricted to the hydrothermally-altered rocks in the deposit area (Fig. 12K). Despite a relatively limited spatial extent, the potassium alteration halo displays a sharp contrast with background metasedimentary rocks, as reflected by elevated values of $Z_{\Delta K_2O}^*$ (1.2) for samples from within the open-pit (Fig. 12K). The few K₂O anomalies ($Z_{\Delta K_2O}^* > 1$) outside of the deposit correspond to weakly mineralized hydrothermal centers (e.g., Cartier, Radium, Alpha and Bravo zones). The mass change values for LOI also define a laterally extensive anomaly that extends parallel to the S₂ foliation along the Cadillac-Larder Lake Fault Zone (Fig. 12L). This anomaly is interpreted to be controlled predominantly by the combined effects of carbonate and sulfide alteration, as reflected by broad similarities in the mass change distribution patterns for these variables (Fig. 12I-J,L).

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released during replacement of plagioclase by microcline (Helt et al., 2014; Gaillard et al., 2018). These observations suggest a significant control on the nature of the alteration assemblage by host-rock compositions. As such, alkali metasomatism was likely limited by Al contents, as K- and Na-bearing phases in the alteration assemblage are characterized by alkali/aluminium molar element ratios ≤ 1 (Mathieu, 2018).

The above reactions (6, 7 and 8) are consistent with a progressive increase in fO_2 , $\sum aS$ and pH conditions with increasing degrees of hydrothermal fluid-rock interaction. The mineralogical reactions that control alkali metasomatism therefore contribute to the delineation of a sulfidation-oxidation halo around the fluid pathways, in agreement with the conclusions of Gaillard et al. (2018). Such mineralogical transitions also support a potassium- and sulfur-rich, oxidized composition for the ore-forming fluids.

10.2. Controls on the distribution of the metasomatic processes

The results of mass change calculations were examined to determine the distribution of hydrothermal fluid-rock interaction in the Malartic district (Fig. 12). This information was used to outline the patterns and maximum extent of the metasomatic haloes associated with ore-forming processes. The lithogeochemical anomalies display large variations in size and magnitude among the variables, which were affected by the composition of the mineralizing fluids, and differences in the mobility and reactivity of alteration-related elements. The above notwithstanding, most alteration haloes have similar geometries, and define elongate envelopes that extend parallel to the main (S_2) foliation (Fig. 12).

The distribution of mass transfer processes depends on several criteria, foremost among which are the structural features that controlled the circulation of the mineralizing fluids. At Canadian Malartic, the main ore-stage is interpreted to have been synchronous with the D_2 deformation event, and the ore zones display a strong spatial association with D_2 structures including the Sladen fault, and the NW-SE deformation zones (Fig. 3; Sansfaçon, 1986; De Souza et al., 2016). At the district scale, this association is manifested by the consistent distribution of the gold showings (weakly mineralized) along strike with the S_2 foliation (Fig. 2). Most of the lithogeochemical anomalies, notably those delineated by the pathfinder trace elements, reflect this structural control and form elongated haloes that extend parallel to the S_2 fabric (Fig. 12).

The geometry of the metasomatic envelopes may also be affected by the superposition of metamorphic and/or deformation events. At Canadian Malartic, gold mineralization is interpreted to have formed early- to syn-peak metamorphism (M_2) (Gaillard et al., 2018). For this reason, it is possible that the alteration

footprint associated with ore-forming processes was modified during metamorphism, which increased in grade from upper greenschist facies adjacent to the deposit, to mid-amphibolite facies a few kilometers to the south (Fig. 2). Most significantly, the transition from greenschist to amphibolite facies is generally associated with a series of devolatilization reactions, which typically coincide with a release of sulfur associated with the conversion of pyrite to pyrrhotite (Pitcairn et al., 2006; Phillips and Powell, 2010; Gaillard et al., in review). The latter reaction may also play a critical role in the liberation of pyrite-hosted trace metals (e.g., Au and related elements) to the metamorphic fluids (Pitcairn et al., 2010). In the Malartic district, devolatilization associated with increasing metamorphic grade likely contributed to a southward decrease in the concentrations of these elements in the background metasedimentary rocks (Fig. 12). Most notably, loss on ignition (LOI), sulfur and carbon, as well as metals liberated during pyrite (e.g., Au, As, Te, Bi) and Fe-Ti oxide (e.g., W, Sb) breakdown represent variables that may have been mobilized along the metamorphic gradient.

10.3. Implications for mineral exploration

The results of mass transfer calculations display a progressive increase in the concentrations of C-S-K₂O and LOI, as well as Au-Te-W-Ag±(As-Be-Sb-Bi-Mo-Pb) from background to distal and proximal alteration zones (Figs. 8-9). Enrichment patterns are shown to delineate broad metasomatic envelopes around the deposit, and were used to trace the location of hydrothermal fluid-rock interaction in the Malartic district (Fig. 12). The statistical approach based on the comparison of the mass balance results with the background composition provides robust constraints on the magnitude and extent of the lithogeochemical haloes. Here, we use this information to identify the components that are most likely to provide exploration vectors towards gold mineralization.

The pathfinder elements define extensive alteration footprints around the Canadian Malartic deposit, in sharp contrast with the background metasedimentary rocks (Fig. 12A-G). The anomalies delineated by Au, Te, W and Ag form the largest metasomatic haloes, reaching up to 10 km in length and 2 km in width (Fig. 12A-D). Because they display a strong metasomatic signal and are only weakly affected by outliers, W, and to a lesser extent, Te and Ag, provide the best vectors towards gold mineralization. By contrast, other pathfinder elements, including As, Be and Sb form generally asymmetric haloes around the deposit, and display several false positive anomalies, thereby hindering potential applications as ore-vectoring tools (Fig. 12E-H). Carbon, S and LOI outline district-scale geochemical haloes enveloping gold mineralization;

however, these variables are also affected by the presence of outliers that obscure gradients toward hydrothermal centers (Fig. 12I-J,L). Finally, the potassic halo defined by K₂O enrichment provides a useful proxy for hydrothermal alteration, although it is mainly restricted to the immediate deposit area (Fig. 12K).

The mass transfer data for the Malartic district represent compositional vectors that can also be applied more widely for gold exploration in metamorphic terranes. In fact, the Au-Te-W-Ag±(As-Sb-Bi-Mo-Pb) signature of the ore assemblage displays strong similarities with other intrusion-related and orogenic-type gold deposits (Robert and Poulsen, 1997; Brauhart et al., 2017). Notably, W, Te and Ag have also been shown to provide vectors toward gold mineralization in the Red Lake (Stock, 2012) and Norseman-Wiluna (Eilu and Groves, 2001; Prendergast, 2007) greenstone belts, and in the Lachlan fold belt (Bierlein et al., 2000). In these locations, pathfinder elements were used to detect the cryptic effects of alteration a few tens of meters, and more rarely up to several kilometers away from the fluid corridors.

The nature of hydrothermal alteration varies as a function of host-rock lithology (Bierlein et al., 2000). A companion study conducted by Perrouy et al. (2018) on mafic dykes is used to assess such lithological controls on alteration processes in the Malartic district. A comparison of the lithogeochemical anomalies in mafic dykes and metasedimentary rocks shows several differences in the magnitude and distribution of the metasomatic haloes. The results indicate that carbon and alkaline elements (K, Cs, Rb) delineate larger anomalies in the mafic dykes, whereas pathfinder element (W, Te, Ag) anomalies generally extend farther in the metasedimentary rocks. These observations thus suggest a strong lithological control on the chemical reactivity and precipitation of ore-fluid components. This information may be used in mineral exploration to enhance the detection of cryptic alteration through the careful selection of the most reactive target media, and comparison of the results between different rock types.

11. Conclusions

This study demonstrates that whole-rock lithogeochemistry is a valuable tool for mapping the intensity and distribution of hydrothermal alteration in the Malartic district. Mass change results provide insights into metasomatic effects associated with ore-forming processes, and can be used to identify the components that are potentially most useful as vectors to gold mineralization. The signature of the mineralized system is characterized by strong enrichments compared to least altered equivalents in C-S-K₂O-LOI, as well as Au-Te-W-Ag±(As-Be-Sb-Bi-Mo-Pb), with increasing intensities from background, to distal and proximal alteration zones. Molar element ratio analysis also provides a means with which to assess the mineralogical

controls associated with alkali metasomatism (K and Na), and illustrates a progressive increase in the proportions of microcline and albite adjacent to fluid pathways (at the expense of biotite and white mica).

Enrichment patterns defined by pathfinder elements outline broad lithogeochemical anomalies around the deposit, and can be used to trace hydrothermal fluid-rock interaction in the district. The alteration haloes generally consist of elongate envelopes oriented parallel to the foliation (S_2), with a lateral extent reaching up to several kilometers away from the deposit. Notably, Au, W, Te and Ag delineate the largest anomalies, and define semi-continuous alteration footprints reaching approximately 10 km in length and 2 km in width. These results demonstrate that the lithogeochemical approach provides a valuable vectoring tool toward gold mineralization in metamorphic terranes, and can be used to recognize even cryptic alteration associated with ore-forming processes at the district-scale.

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FIGURES

Figure 1: A regional lithostratigraphic map of the Abitibi and Pontiac subprovinces showing the locations of the main ore deposits along the Rouyn-Val d'Or segment (modified from [Bedeaux et al., 2017](#); compiled from [Hubert et al., 1984](#); [Imreh, 1984](#); [Desrochers and Hubert, 1996](#)). Individual deposits are represented by colored circles that are scaled according to metal endowment, as calculated from past production and current reserve estimates (compiled from [Rafini \(2014\)](#), and references therein). Abbreviations: CLLFZ: Cadillac-Larder Lake Fault Zone; DPMFZ: Destor-Porcupine-Manneville Fault Zone; PFZ: Parfouru Fault Zone.

Figure 2: A lithostratigraphic map of the Malartic district showing the main structural, metamorphic and lithological features of the study area (modified from [Perrouy et al., 2017](#); compiled from [Derry, 1939](#); [Gunning and Ambrose, 1943](#); [Minerais Lac Limited maps](#); [Sansfaçon et al., 1987a,b](#); [Fallara et al., 2000](#); [SIGEOM database, 2016](#); and references therein). The Canadian Malartic open-pit mine is delineated by a yellow outline. The map also displays the locations of the past-producing mines and gold occurrences. UTM Coordinate system NAD83-17N. Abbreviation: CLLFZ: Cadillac-Larder Lake Fault Zone.

Figure 3: A geological map of the Canadian Malartic gold deposit (modified from Gaillard *et al.*, 2018; compiled from MERN geological map CG-32D01D, Pilote, 2014; Perroux *et al.*, 2017; Canadian Malartic Corporation reports; and this study). Gold mineralized zones are projected from elevation $z=300\pm 10$ m. Ore distribution is controlled predominantly by three structures, namely the Sladen and Barnat faults, and the NW-SE deformation zones. Abbreviation: CLLFZ: Cadillac-Larder Lake Fault Zone.

Figure 4: Representative characteristics of the host Pontiac Group metasedimentary rocks. **A:** A flyschoid sequence composed of mudstone to greywacke interstratified beds. The rocks were affected by F_2 folding and display a strong pervasive axial-planar foliation (S_2). **B:** Local effects of the primary compositional variations on the mineralogy of the metamorphic assemblage in a planar-stratified turbiditic sequence. The staurolite porphyroblasts are restricted to the fine-grained pelitic beds (mudstone). **C:** A thin section image showing the textural characteristics of greywacke. The clastic particles of quartz and plagioclase reach up to 1 mm in diameter. **D:** A thin section image of a micro-folded (F_2) sedimentary contact (S_{0-1}). White mica is developed preferentially in the finer-grained, more aluminous mudstone. **E:** A thin section image showing the textural characteristics of mudstone. Detrital quartz and plagioclase grains are typically $<50\ \mu\text{m}$ across. Abbreviations: bt: biotite; Gre: greywacke; ms: muscovite; Mud: mudstone; pl: plagioclase; qz: quartz; silt: Siltstone; st: staurolite.

Figure 5: Representative characteristics of proximal and distal hydrothermal alteration assemblages in the metasedimentary rocks of the Canadian Malartic deposit. **A-B:** Proximal alteration is characterized by a beige/brown microcline±albite-quartz replacement-type assemblage, with subordinate phlogopite, carbonate (calcite±Fe-dolomite), pyrite and rutile. This facies typically occurs in the form of a pervasive alteration envelope around ore-stage (v2) veinlets. **C-D:** Distal alteration consists of a blue/grey assemblage dominated by biotite, microcline±albite, phengite, quartz, calcite, pyrite and rutile. The mineralogy of the distal alteration is controlled in part by variations in protolith grain size; phengite alteration is generally best-developed in fine-grained mudstone layers. Abbreviations: ab: albite; bt: biotite; mic: microcline; ph: phengite; py: pyrite; qz: quartz.

Figure 6: A compilation of box and whisker plots showing primary whole-rock lithogeochemical variations (for major elements) among the main grain size fractions of the Pontiac Group metasedimentary rocks (background population; $n=443$). The samples were separated into four sub-lithologies, namely greywacke (dark blue; $n=171$), siltstone (medium blue; $n=87$), mudstone (green; $n=159$) and low ΣREE (grey; $n=26$) rocks. The sediment compositions display generally clear and systematic variations with decreasing grain size.

Figure 7: *A: A positive correlation ($r=0.78$) between Al_2O_3 and TiO_2 bulk-rock concentrations (in wt.%) suggests a strong cogenetic relationship for the Pontiac Group metasedimentary rock samples ($n=596$). The linear trend between Al_2O_3 and TiO_2 concentrations further indicates that these elements remained immobile during alteration. B: Chondrite-normalized REE patterns (Sun and McDonough, 1995) for the Pontiac Group greywacke ($n=247$), siltstone ($n=134$) and mudstone ($n=188$) fractions are nearly identical and differ only in the absolute distribution of the REE. A separate group is defined by low ΣREE concentrations ($n=27$) and a distinct chondrite-normalized REE profile.*

Figure 8: A compilation of box and whisker diagrams illustrating mass changes produced by hydrothermal alteration for select major elements in the metasedimentary rocks of the Malartic district. The samples were divided into three categories according to alteration characteristics, from background (in purple), to distal (in green) and proximal (in orange) alteration zones.

Figure 9: A compilation of box and whisker diagrams illustrating mass changes produced by hydrothermal alteration for select trace elements in the metasedimentary rocks of the Malartic district. The samples were divided into three categories according to alteration characteristics, from background (in purple), to distal (in green) and proximal (in orange) alteration zones.

	Au	K	Na	K+Na	Ca	LOI	C	S	Ag	As	Be	Bi	Cu	Mo	Pb	Sb	Se	Te	W
Au	1																		
K	0.35	1																	
Na	0.24	-0.29	1																
K+Na	0.51	0.62	0.54	1															
Ca	0.32	-0.02	0.41	0.28	1														
LOI	0.53	0.57	0.04	0.50	0.40	1													
C	0.51	0.49	0.19	0.56	0.51	0.84	1												
S	0.66	0.56	0.29	0.72	0.35	0.75	0.64	1											
Ag	0.62	0.45	0.19	0.55	0.28	0.66	0.54	0.82	1										
As	0.03	0.14	-0.11	0.06	0.05	0.19	0.14	0.10	0.07	1									
Be	0.58	0.63	0.19	0.69	0.31	0.74	0.70	0.70	0.59	0.10	1								
Bi	0.48	0.43	0.14	0.47	0.24	0.60	0.46	0.72	0.57	0.02	0.57	1							
Cu	0.06	0.02	0.01	0.02	0.17	0.10	0.02	0.17	0.19	-0.02	0.09	0.00	1						
Mo	0.22	0.28	0.09	0.31	0.19	0.40	0.29	0.41	0.37	-0.01	0.39	0.65	-0.14	1					
Pb	0.34	0.35	0.20	0.47	0.18	0.45	0.41	0.50	0.44	0.00	0.53	0.64	-0.06	0.50	1				
Sb	0.20	0.31	0.09	0.35	0.19	0.40	0.36	0.43	0.31	0.28	0.27	0.24	0.04	0.11	0.16	1			
Se	0.32	0.32	0.19	0.44	0.31	0.41	0.42	0.59	0.43	0.08	0.45	0.44	0.35	0.23	0.36	0.24	1		
Te	0.66	0.55	0.21	0.65	0.28	0.70	0.60	0.87	0.94	0.07	0.68	0.64	0.11	0.39	0.50	0.32	0.44	1	
W	0.64	0.38	0.28	0.56	0.28	0.53	0.49	0.63	0.59	0.01	0.53	0.43	0.00	0.22	0.38	0.19	0.28	0.70	1

Figure 10: Pearson correlation matrix of the mass change values (enrichment factors) calculated for select major and trace elements in the metasedimentary rocks of the Malartic district (n=596).

Figure 11: Binary plots of alkali/aluminium molar ratios (Na/Al vs. K/Al) for background and altered metasedimentary rocks of the Malartic district ($n=596$). **A:** The effects of primary sedimentary features on whole-rock molar element ratios. Samples are grouped into four categories based on lithological characteristics, namely greywacke (dark blue), siltstone (medium blue), mudstone (green) and low ΣREE (grey) metasedimentary rocks. **B:** The effects of hydrothermal alteration on whole-rock molar element ratios. The samples are grouped into three categories based on alteration characteristics, from background (purple), to distal (green) and proximal (orange) alteration zones. Bold lines for biotite and white mica represent the range of mineral compositions determined from electron microprobe analyses (Gaillard *et al.*, 2018). Abbreviations: alt: altered; met: metamorphic.

Figure 12: A series of interpolated lithogeochemical maps illustrating mass changes associated with hydrothermal alteration in the metasedimentary rocks of the Malartic district. The mass change results for Au (A), Te (B), W (C) and Ag (D) are expressed in terms of standard deviation distance relative to the background population mean (Z^*). See text for details on the calculation method.

Figure 12 (continued): A series of interpolated lithogeochemical maps illustrating mass changes associated with hydrothermal alteration in the metasedimentary rocks of the Malartic district. The mass change results for As (E), Be (F), Sb (G) and Pb (H) are expressed in terms of standard deviation distance relative to the background population mean (Z^*). See the text for details on the calculation method.

Figure 12 (continued): A series of interpolated lithogeochemical maps illustrating mass changes associated with hydrothermal alteration in the metasedimentary rocks of the Malartic district. The mass change results for C (I), S (J), K_2O (K) and LOI (L) are expressed in terms of standard deviation distance relative to the background population mean (Z^*). See the text for details on the calculation method.

APPENDICES

Appendix 1: A compilation of box and whisker plots showing the primary whole-rock lithogeochemical variations (for minor elements) among the main grain size fractions of the Pontiac Group metasedimentary rocks (background population; $n=443$). The samples were separated into four sub-lithologies, namely greywacke (dark blue; $n=171$), siltstone (medium blue; $n=87$), mudstone (green; $n=159$) and low Σ REE (grey; $n=26$) sediments. The bulk-rock sediment compositions are shown to display systematic variations with decreasing grain size.

	Au	K	Na	K+Na	Ca	LOI	C	S	Ag	As	Be	Bi	Cu	Mo	Pb	Sb	Se	Te	W
Au	1																		
K	0.55	1																	
Na	0.08	-0.39	1																
K+Na	0.67	0.50	0.48	1															
Ca	0.24	-0.19	0.47	0.29	1														
LOI	0.66	0.54	-0.14	0.41	0.15	1													
C	0.70	0.48	0.09	0.56	0.32	0.77	1												
S	0.65	0.39	0.19	0.62	0.25	0.59	0.52	1											
Ag	0.80	0.48	0.19	0.67	0.28	0.65	0.62	0.80	1										
As	0.54	0.29	0.01	0.32	0.18	0.44	0.54	0.43	0.44	1									
Be	0.70	0.54	0.10	0.67	0.20	0.73	0.74	0.54	0.61	0.38	1								
Bi	0.53	0.34	0.11	0.40	0.15	0.53	0.42	0.66	0.67	0.28	0.42	1							
Cu	-0.06	-0.01	-0.05	-0.10	0.01	-0.03	-0.08	0.22	0.07	0.03	-0.08	-0.05	1						
Mo	0.34	0.38	0.07	0.37	-0.05	0.32	0.29	0.30	0.37	0.10	0.34	0.44	-0.16	1					
Pb	0.50	0.31	0.22	0.59	0.22	0.48	0.56	0.52	0.56	0.25	0.63	0.47	-0.13	0.34	1				
Sb	0.45	0.26	0.06	0.34	0.20	0.37	0.41	0.41	0.45	0.49	0.26	0.27	0.03	0.13	0.25	1			
Se	0.37	0.26	0.12	0.39	0.22	0.41	0.34	0.62	0.49	0.26	0.41	0.46	0.20	0.29	0.41	0.25	1		
Te	0.82	0.54	0.12	0.69	0.21	0.66	0.64	0.75	0.88	0.41	0.67	0.67	-0.04	0.39	0.55	0.38	0.50	1	
W	0.78	0.43	0.28	0.67	0.27	0.57	0.61	0.60	0.71	0.44	0.60	0.50	-0.06	0.35	0.44	0.44	0.35	0.71	1

***Appendix 2:** Pearson correlation matrix of log-transformed mass change values (enrichment factors) calculated for select major and trace elements in the metasedimentary rocks of the Malartic district (n=596).*