Tourmaline, scheelite, and magnetite compositions from orogenic gold deposits and glacial sediments of the Val-d’Or district (Québec, Canada): applications to mineral exploration

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Abstract

Tourmaline, scheelite, and magnetite from orogenic gold deposits \((n = 22)\) and glacial sediments \((n = 5)\) of the Val-d’Or mining district (Québec, Canada) were investigated by Electron Probe Micro-Analyzer (EPMA) and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) in order to determine their chemical signature and to assess their potential as indicator minerals for gold exploration. Three types of tourmaline are recognized. Type I tourmaline from deposits hosted in felsic and intermediate-composition calc-alkaline rocks has low contents of V, Cr, Mn, Fe, Co, Ni, Zn, and Sn and a high content of Mg compared to Type II tourmaline from deposits hosted in mafic tholeiitic rocks. Type III tourmaline from deposits located at the contact between mafic metavolcanic and metasedimentary rocks shows a chemistry similar to Type I tourmaline with slightly higher Li, Mn, and Pb contents. Tourmaline from orogenic gold deposits is characterized by lower contents of Zn, Cu, Sn, and Pb compared to data from tourmaline associated with Cu-Zn, Pb-Zn-Cu, and Sn mineralization. Till tourmaline carries the chemical signature of that from orogenic gold deposits with a majority having the signature of Type I tourmaline. Orogenic gold deposits scheelite from the Val-d’Or district hosted in calc-alkaline intrusions of intermediate composition displays high Na, REE, and Y contents compared to scheelite from sediment- and mafic-hosted gold deposits. Till scheelite carries the chemical signature of that from orogenic gold deposits. Although rare in orogenic gold deposits of the Val-d’Or district, hydrothermal magnetite in the gold veins is characterized by higher Cr, Zn, Mn, K, Ca, Ti, and Al than magmatic magnetite found in dioritic and gabbroic host rocks. Magnetite associated with gold mineralization forms fine, disseminated grains, suggesting that the coarse-grained magnetite recovered in till does not originate from the gold veins. Till tourmaline and scheelite carry the signature of the orogenic gold deposits and can thus be used for exploration in overburden sediments.

Keywords: Tourmaline, scheelite, magnetite, mineral chemistry, orogenic gold deposits

Highlights:

- Till tourmaline has the same compositional signature as orogenic gold tourmaline
- Till scheelite is chemically similar to orogenic gold scheelite
- Till magnetite does not originate from the Val-d’Or gold deposits
- Tourmaline and scheelite in till are good indicator minerals for orogenic gold deposits
1. Introduction

The indicator mineral technique has grown significantly since the 1980s and has been successfully used in mineral exploration for several types of deposits, including diamond-bearing kimberlite, lode gold, magmatic Ni-Cu-PGE, Cu porphyry, volcanogenic massive sulfide (VMS), Mississippi Valley-Type (MVT), W-Mo porphyry, skarn, and greisen (Averill 2001; Heimann et al. 2005; McClenaghan 2005; McClenaghan and Kjarsgaard 2007; Averill 2011; Kelley et al. 2011; McClenaghan and Cabri 2011; Oviatt et al. 2013; Paulen et al. 2011; McClenaghan et al. 2014; Lehtonen et al. 2015, Manéglia et al. 2018). The indicator mineral technique was successfully used to discover gold deposits such as Golden Pond East and West at Casa Berardi, Québec (Sauerbrei et al. 1987), Aquarius in Timmins, Ontario (Gray 1983), and 17 Zone in Rainy River, Ontario (Averill 2001).

Orogenic gold deposits represent 45% of gold deposits worldwide containing more than 1 Moz of gold, which is more than intrusion-related deposits (28%), epithermal deposits (24%), and paleoplacers (3%) (Goldfarb et al. 2005). In Canada, orogenic gold deposits constitute 59% of total gold production and reserves (Dubé and Gosselin 2007). Over 95% of Canada’s surface was covered by glaciers during the Pleistocene, making the use of indicator minerals in glacial sediments particularly important for exploration. Gold grains are the best indicator for detecting the presence of gold mineralization; however, other indicator minerals such as sulfides (pyrite, pyrrhotite, arsenopyrite, chalcopyrite, sphalerite, galena, pyrargyrite, proustite, and cinnabar), platinum-group minerals, tellurides, scheelite, cassiterite, and rutile may also be useful depending on the deposit type, bedrock geology, and weathering regime of the area (McClenaghan and Cabri 2011). In orogenic gold deposits of the Val-d’Or district, tourmaline, scheelite, and magnetite occur as common or accessory minerals within the gold-bearing quartz-tourmaline-carbonate veins and are preserved in local glacial sediments. The physical and chemical characteristics of these minerals, such as resistance to weathering, hardness, variable chemistry, etc., make them potential indicators in the exploration for orogenic gold deposits.

Given that tourmaline, scheelite, and magnetite occur in diverse rock types and mineral deposits, characterizing their chemical signature (major, minor, and trace elements) in orogenic gold deposits is necessary in order to identify the provenance of tourmaline, scheelite, and magnetite recovered in glacial sediments of the Val-d’Or district. Although the major element composition of tourmaline from various deposit and rock types has been the focus of numerous studies, trace element data on tourmaline are more limited (Taylor and Slack 1984; Slack and Coad 1989; Griffin et al. 1996; Slack et al. 1999; Yavuz 1999; Jiang et al. 2002, Jiang et al. 2004; Galbraith et al. 2009; Roberts et al. 2006; Mark et al. 2013; Chapman et al. 2015; Hazarika et al. 2015, 2016; Duchoslav et al. 2017; Kalliomäki et al. 2017; van Hinsberg et al. 2017; Harlaux et al. 2018; Manéglia et al. 2018). Most studies on scheelite focus on understanding the partitioning and distribution of contained REE, with limited studies carried on trace elements (Cottrant 1981; Brugger et al. 2000a, b; Roberts et al. 2006; Dostal et al. 2009; Song et al. 2014;
Hazarika et al. 2016; Poulin 2016). Compared to tourmaline and scheelite, trace elements in magnetite from diverse ore deposits have been the subject of numerous studies (Dupuis and Beaudoin 2011; Dare et al. 2012, 2014; Boutroy et al. 2014; Nadoll and Mauk 2011; Nadoll et al. 2012, 2014, 2015; Makvandi et al. 2016a, b), but these studies did not report on orogenic gold deposit magnetite.

Here, we use the major, minor, and trace element composition of tourmaline, scheelite, and magnetite from orogenic gold deposits to identify discriminant criteria based on binary and ternary diagrams and Principal Component Analysis (PCA). We also compare the composition of tourmaline, scheelite, and magnetite recovered from glacial sediments with the chemistry of indicator minerals from the Val-d’Or gold-bearing quartz veins in order to determine their provenance and evaluate the use of tourmaline, scheelite, and magnetite as indicator minerals for gold exploration in glaciated terrains.

2. Geological setting
2.1 Regional geology

The Val-d’Or district is located along the eastern segment of the southern volcanic zone (Ludden et al. 1986; Chown et al. 1992; Daigneault et al. 2002) at the boundary between the Abitibi and Pontiac subprovinces of the Superior Province (Fig. 1; Card 1990). The volcano-sedimentary Abitibi and metamafic sedimentary Pontiac subprovinces are separated by the Larder Lake-Cadillac Fault Zone (LLCFZ), a crustal-scale shear zone extending more than 200 km along strike (Robert et al. 1995).

The Val-d’Or district consists of a complex volcano-sedimentary sequence of ultramafic to felsic metavolcanic rocks erupted between 2714 ± 2 Ma and 2702 ± 2 Ma (Pilote et al. 2000; Scott et al. 2002), known as the Malartic and Louvicourt groups. The metavolcanic rocks are overlain by minor metamafic sedimentary rock assemblages, which include the Lac Caste Formation (<2691 ± 8 Ma; Feng and Kerrich 1991), Cadillac Group (<2688 Ma; Davis 1991), and Kewagama Formation (<2687 Ma; Davis 1991). The Malartic Group comprises the La Motte-Vassan, Dubuisson, and Jacola formations that consist of komatiitic and tholeiitic basaltic flows and sills interpreted to have formed an Archean oceanic floor controlled by extensional mantle-plume tectonics (Desrochers et al. 1993; Scott et al. 2002). The Val-d’Or and Héva formations of the Louvicourt Group consist of mafic to felsic metavolcaniclastic and metavolcanic rocks that formed in a volcanic arc (Daigneault et al. 2002; Scott et al. 2002). The Cadillac Group comprises metamorphosed graywacke, pelitic schist, polymictic conglomerate, and iron formation (Imreh 1984) interpreted as a syn-orogenic flysch-type assemblage (Daigneault et al. 2002; Mueller et al. 1996). The Lac Caste and Kewagama formations represent an inter-arc turbidite sequence, which is part of the flysch basin system linking the northern volcanic zone with the southern volcanic zone (Daigneault et al. 2002). Syn-volcanic to post-tectonic mafic to felsic bodies intruded the volcano-sedimentary sequence of the Val-d’Or
district during three main events: synvolcanic stocks and batholiths (2706 ± 1 Ma to 2700 ± 1 Ma; e.g., Bourlamaque batholith; Wong et al. 1991; Pilote et al. 2000), syn- to late-tectonic intrusions (2694 ± 2 Ma to 2680 ± 2 Ma; Jemielita et al. 1990; Morasse et al. 1993; Wong et al. 1991; Pilote et al. 2000), and undeformed late- to post

tectonic stocks and dikes (2675 Ma to 2611 Ma; Feng and Kerrich 1991; Feng et al. 1992). South of the LLCFZ, the Pontiac Group (<2685 ± 3 Ma; Davis 2002) consists of metamorphosed graywacke and mudstone intercalated with ultramafic metavolcanic rocks (Dimroth et al. 1982; Ludden et al. 1986; Pilote et al. 2000).

All rocks, with the exception of late stocks and dikes, were metamorphosed to greenschist facies between 2693 ± 11 Ma (Hanes et al. 1992) and 2677 ± 6 Ma (Feng et al. 1992). Metamorphic grade gradually increases southward from upper greenschist facies along the LLCFZ to amphibolite facies in the Pontiac Subprovince. Three major phases of deformation have been recognized in the Val-d’Or district. During the first phase of deformation (D1), several mafic to ultramafic tectonostratigraphic terranes were accreted to form the Malartic composite block. Desrochers and Hubert (1996) suggested that the calc-alkaline felsic metavolcanic and volcanoclastic rocks of the Val-d’Or Formation overly unconformably the Malartic composite block. Scott et al. (2002), however, described the Val-d’Or Formation as having a concordant contact with the underlying Jacola Formation, indicating a change from tholeiitic mafic volcanoclastic to calc-alkaline flows and volcanoclastic rocks of intermediate to felsic composition. The tholeiitic mafic to felsic flows and volcanoclastic rocks of the Héva Formation form a stratigraphic continuum with the underlying Val-d’Or Formation. A second phase of deformation (D2) produced the dominant subvertical E-W foliation, faults, and shear zones that host most of the gold-bearing quartz veins as a result of a N-S compressional event (Dimroth et al. 1983a, b; Robert 1989; Desrochers and Hubert 1996). Deformation ended with dextral transcurrent movement (D3) that reactivated the LLCFZ and several second-order shear zones (Robert et al. 1995; Neumayr et al. 2000).

2.2 Gold mineralization

Based on crosscutting relationships, two generations of shear zone-related gold-quartz veins are recognized in the Val-d’Or district. Early quartz-carbonate veins (≥2686 Ma) are mainly associated with second-order shear zones and are cut by 2694 to 2680 Ma syntectonic dikes of tonalitic to dioritic composition (Couture et al. 1994; Robert et al. 1995). Early quartz-carbonate veins (e.g., Norlartic, Siscoe, Callahan) are commonly folded and boudinaged within sub-vertical shear zones as a result of D2 deformation (Sauvé et al. 1993; Robert et al. 1995). Younger (≤2684 Ma) quartz-tourmaline-carbonate veins (e.g., Sigma, Lamaque, Beaufor) developed in the late stages of D2 shortening and form either subvertical fault-fill or subhorizontal extensional veins; they are typically associated with third-order shear zones and cut all intrusive rocks.
The plutonic and metavolcanic rocks of the Val-d’Or district host most of the gold-bearing quartz veins, although some veins also occur within metasedimentary rocks of the Pontiac Subprovince. Gold deposits rarely occur in first-order shear zones such as the LLCFZ, with the exception of a few mines and prospects such as Lapa and Orenada (Simard et al. 2013; Desrochers and Robert 2000; Neumayr et al. 2000). Gold mineralization within the LLCFZ occurs as disseminated gold associated with arsenopyrite. Other gold deposits, such as Kiena (Morasse et al. 1995) and Akasaba (Robert and Brown 1986b), are interpreted as porphyry-gold and skarn mineralization, respectively.

2.3 Quaternary geology

During the last 2 m.y., several glaciations such as the Nebraskan, Kansan, Illinoian, and Wisconsinan have shaped the surface of the Abitibi Subprovince. The most distinct glacial footprint on the current landscape resulted from the complex sequence of ice flows that formed during the Wisconsinan glaciation (Veillette and McClenaghan 1996; McClenaghan 2001). However, signs of previous glaciations are also recorded on the surface of bedrock. The initial ice flow (flow I) of the Wisconsinan glaciation was oriented toward the northeast during the early expansion of the Laurentide Ice Sheet (Veillette 1995). Ice flow orientation shifted counterclockwise toward the west (flow II), the southwest (flow III), and the south-southwest (flow IV) during the main phase of the Laurentide Ice Sheet. During deglaciation, the glacier was divided into two lobes with an opening that resulted in deposition of the Lake McConnell and Harricana interlobate moraines. From either side of the opening in the ice sheet, ice flow (flow V) was converging (Veillette and McClenaghan 1996; Paradis 2007) toward the southeast on the west side of the opening and to the southwest on the east side. The Cochrane surge (flow VI) is recorded by the youngest striations, oriented toward the south, southeast, and east-southeast, extending from the James Bay region to the area where glacial Lake Ojibway formed. The Matheson till, deposited during the Wisconsinan glaciation, is overlain by thick (5 to 30 m) glaciolacustrine silt and clay deposits that accumulated in glacial Lake Ojibway, Cochrane till, and extensive peatland (Veillette 1995; McClenaghan 2001). The till sampling area of this study, east of Val-d’Or, was only affected by ice flow V oriented toward the south and southwest (Fig. 1).

2.4 Mineralogy

Tourmaline is a complex boron-rich cyclosilicate that occurs as a major or accessory mineral in diverse types of sedimentary, igneous, and metamorphic rocks and in a variety of hydrothermal and magmatic ore deposits (Slack 1996; Slack and Trumbull, 2011; van Hinsberg et al. 2011a). Tourmaline forms over a significant range of pressures (<0.06 to >6 GPa) and temperatures (<150 to > 950°C) in various geological settings (Dutrow and Henry
and has a distinctive chemical signature reflecting a wide array of major, minor, and trace elements (Henry et al. 2011). Minerals of the tourmaline supergroup share the general chemical formula \( XY_3Z_6(T_6O_{18})(BO_3)_3V_3W \), with site occupancies as follow: \( X = Ca^{2+}, Na^+, K^+, \) and vacancy; \( Y = Ti^{4+}, Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, \) and Li\(^+\); \( Z = Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mg^{2+}, \) and Fe\(^{2+}\); \( T = Si^{4+}, Al^{3+}, \) and B\(^{3+}\); \( B = B^{3+}; V = O^2- \) and OH\(^-\); and \( W = O^2-, OH^-, F^-, \) and Cl\(^-\) (Hawthorne and Henry 1999). The best-known species of the tourmaline supergroup are dravite (NaMg\(_3\)Al\(_6\)Si\(_6\)O\(_{18}\)(BO\(_3\))\(_3\)OH\(_4\)), schorl (NaFe\(_3\)Al\(_6\)Si\(_6\)O\(_{18}\)(BO\(_3\))\(_3\)OH\(_4\)), and elbaite (Na(Li,Al)\(_3\)Al\(_6\)Si\(_6\)O\(_{18}\)(BO\(_3\))\(_3\)OH\(_4\); Dutrow and Henry 2011; Henry et al. 2011). Concentrations of major, minor, and trace elements in tourmaline are controlled by (1) fluid/rock interaction; (2) fluid composition, flux, mixing, and boiling; (3) composition of the host rock; (4) element partition coefficient between tourmaline, fluids and co-forming minerals; (5) temperature; (6) pressure; and (7) redox state (Griffin et al. 1996; Slack and Trumbull 2011). Its complex and variable chemistry, coupled with negligible intracrystalline element diffusivity, allow tourmaline to record and preserve the chemical signature of its host environment, making it an ideal indicator mineral (van Hinsberg et al. 2011b). Moreover, chemical stability and physical characteristics such as specific gravity (2.9-3.2), hardness (7.0-7.5), and lack of cleavage make tourmaline a robust mineral highly resistant to weathering and transport in clastic sediments (Hawthorne and Dirlam 2011).

Scheelite is a calcium tungstate occurring as a common or accessory mineral in various types of magmatic and hydrothermal ore deposits including pegmatite, greisen, Sn-W vein, porphyry, skarn, VMS, epithermal, and orogenic gold (Hsu and Galli 1973; Kontak et al. 2015; Poulin 2016). Scheelite crystallizes at pressures ranging from 0.02 to 0.15 GPa and temperatures between 200 and 500 °C (Wood and Samson 2000). Low oxygen and sulfur fugacity conditions are necessary for scheelite crystallization (Brugger et al. 1998). Scheelite has the basic chemical formula \( CaWO_4 \), and its crystal structure has two unique cation sites: an [8]-coordinated site, in which \( Ca^{2+} \) may be replaced by \( Sr^{2+}, Pb^{2+}, Fe^{3+}, Mn^{2+}, Ba^{2+}, \) and REE\(^{3+} \); and a [4]-coordinated site, in which Mo\(^{6+}, As^{5+}, \) and Nb\(^{5+} \) can substitute for W\(^{6+} \) (Ghaderi et al. 1999; Raimbault et al. 1993). Scheelite forms a complete solid solution series with powellite (CaMoO\(_4\)). Substitution of trivalent REE for divalent Ca occurs by three coupled substitutions to balance the charge difference: (1) \( 2Ca^{2+} = REE^{3+} + Na^+ \), (2) \( Ca^{2+} + W^{6+} = REE^{3+} + Nb^{5+} \), and (3) \( 3Ca^{2+} = 2REE^{3+} + Ca\)-site vacancy (Ghaderi et al. 1999). The composition of major, minor, and trace elements in scheelite is controlled by the same factors as in tourmaline, but with the addition of oxygen and sulfur fugacity (Hsu and Galli 1973; Robert and Brown 1986b). Scheelite is resistant to weathering and may be concentrated in clastic sediments due to chemical stability in surficial environments and physical properties such as specific gravity (5.9-6.1) and hardness (4.5-5.0). However, scheelite is brittle and survives only moderate distances during glacial or fluvial transport (McClenaghan et al. 2015). Characteristic is a strong bluish-white color fluorescence under short ultraviolet radiation (Klein and Dutrow 2008), making scheelite one of the most common indicator minerals used to explore for W, Sn, and Au mineralizations (Averill 2001; McClenaghan 2005).
Magnetite is an iron oxide mineral commonly found in various types of sedimentary, igneous, and metamorphic rocks (Klein and Dutrow 2008) and occurs as a major or an accessory mineral in various deposit types including banded iron formation (BIF), iron oxide-copper-gold (IOCG), Kiruna type magnetite-apatite, Fe-Ti, porphyry, skarn, Ni-Cu-PGE, VMS, Opemiska-type Cu veins, and clastic-dominated Pb-Zn (Heimann et al. 2005; Leach et al. 2010; Dupuis and Beaudoin 2011; Nadoll et al. 2014). Magnetite belongs to the spinel group and is characterized by the basic chemical formula XY$_2$O$_4$, where divalent cations such as Mg, Ni, Mn, Co, and Zn can substitute for Fe$^{2+}$ in the X-site and trivalent cations such as Al, Cr, V, Mn, and Ga may replace Fe$^{3+}$ in the Y-site (Wechsler et al. 1984; Biagioni and Pasero 2014). A tetravalent cation (e.g., Ti$^{4+}$) coupled with a divalent cation can be incorporated in the X- and Y-sites. Minerals from the magnetite series include magnesioferrite (MgFe$_2$O$_4$), franklinite (ZnFe$_2$O$_4$), jacobsite (MnFe$_2$O$_4$), and trevorite (NiFe$_2$O$_4$). Concentrations of major, minor, and trace elements in magnetite are controlled by (1) magma composition, (2) temperature, (3) pressure, (4) cooling rate, (5) fluid composition, (6) oxygen and sulfur fugacity, (7) silica and sulfide activity, (8) ionic radius and overall charge balance of substituting elements, and (9) composition of co-forming minerals and partition coefficients of various substituting elements between competing mineral phases (Buddington and Lindsley 1964; Fleet 1981; Wechsler et al. 1984; Whalen and Chappell 1988; Frost 1991; Frost and Lindsley 1991; Ghiorso and Sack 1991; Haggerty 1991; Cornell and Schwertmann 2003; Mollo et al. 2013; Biagioni and Pasero 2014; Nadoll et al. 2014). Chemical stability in surficial environments and physical properties such as specific gravity (5.1-5.2) and hardness (5.0-6.0) allow magnetite to resist weathering and to be concentrated in clastic sediments (Makvandi et al. 2015). Magnetite is easily separated from the heavy mineral concentrates (HMC) because it has the highest magnetic susceptibility among all naturally occurring minerals.

3. Methodology

3.1 Sample selection

3.1.1 Quartz veins

Six hundred thirty-six mineralized rock samples from 54 gold deposits and prospects in the Val-d’Or district were available for this study (Pitre 2000; Roussy 2003; Rezeau et al. 2017). Samples were collected from subvertical veins in shear zones, subhorizontal extensional veins, and various tectonic and hydraulic breccias hosted in metavolcanic, plutonic, and metasedimentary rocks. Samples were selected to offer a representative distribution of the gold mineralization across the district. One hundred fifty-five representative polished thin sections were described for 34 gold deposits and prospects. Chemical analyses were obtained on indicator minerals from 22 deposits and prospects (Fig. 1; Appendix A).
Tourmaline occurs in quartz veins hosted in various lithologies including: (1) felsic to intermediate-composition calc-alkaline intrusions, (2) mafic plutonic and metavolcanic rocks of tholeiitic affinity, and (3) at the contact between mafic to ultramafic metavolcanic and metasedimentary rocks within the LLCFZ, which are designated as type I, II, and III tourmalines, respectively. In the Val-d’Or district, Type I tourmaline is the most common and occur in several deposits including Beaufor, Canmet (nord), Lac Herbin, Nord-Ouest, and Snowbank hosted within the Bourlamaque batholith, a calc-alkaline quartz-diorite intrusion. Type I tourmaline is also present at the O’Connell deposit hosted in the Connell pluton, an apophysis of the Bourlamaque batholith (Sauvé et al. 1993) and at the Buffadison deposit hosted in the Bevcon pluton, a calc-alkaline intrusion of tonalitic to dioritic composition. Type I tourmaline also occurs at the Audet, Goldex, Lucien Béliveau/New Béliveau, Lamaque Sud, Kiena, and Sigma deposits, which are hosted in various small calc-alkaline intrusions of dioritic composition intruded into metavolcanic rocks. Type II tourmaline occurs at the Sigma 2 and Bloc Sud deposits hosted in a differentiated tholeiitic intrusion of tonalitic to gabbroic composition (Vicour sill), and at the Paramaque deposit hosted in a tholeiitic intrusion of gabbroic composition (Annamaque sill), both located at the contact between the Val-d’Or and Héva formations. Type II tourmaline at the Siscoe deposit is hosted in the Siscoe stock, a homogenous quartz-gabbro intrusion of tholeiitic affinity at the contact with the Dubuisson Formation, and at the Brosnor deposit hosted in tholeiitic metabasalt of the Jacola Formation. Type III tourmaline occurs at the Lapa and Oreneda deposits, both located within the LLCFZ at the contact between metavolcanic rocks of tholeiitic and calc-alkaline affinity (Piché Group) and metasedimentary rocks.

Scheelite was sampled at the Beaufor and Sigma deposits and at the Triangle Zone of the Lamaque Sud gold project. Scheelite from the Sigma and Beaufor deposits occurs in quartz veins hosted in a dioritic intrusion of calc-alkaline affinity, whereas scheelite from the Triangle Zone is in a breccia also hosted in a calc-alkaline dioritic intrusion.

Magnetite is rare in quartz veins of the Val-d’Or district. Hydrothermal magnetite occurs within quartz veins of the Goldex, Sigma, and Louvicourt deposits, whereas hydrothermal hematite is found in the Lac Herbin and Vein No. 5 deposits. Magmatic magnetite occurs in calc-alkaline dioritic host rocks of the Beaufor deposit and in tholeiitic gabbroic host rocks of the Bloc Sud deposit.

### 3.1.2 Glacial sediments

Five glacial sediment samples of 9 to 13 kg were collected east of the city of Val-d’Or, along a 20-km-long transect oriented NE-SW, following the direction of ice flow V (Fig. 1). Each till sample was collected from the C horizon over the Matheson basal till. The northernmost sample (14-DG-001) is located up-ice, north of the district. Samples 14-DG-002, 14-DG-005, and 14-DG-004 are from the transect in the Val-d’Or district. The southernmost sample (14-DG-003) is located down-ice, 4 km south of the LLCFZ, within the Pontiac Subprovince.
3.2 Sample preparation

3.2.1 Heavy mineral concentrates

Representative mineralized rock samples (n = 11) were disaggregated using a CNT-MC Inc.’s Spark 2 Electric-Pulse Disaggregator (EPD) to liberate minerals. HMC of mineralized rocks and glacial sediments were prepared by Overburden Drilling Management Ltd (Ottawa). Glacial sediments and disaggregated mineralized rock samples were sieved (wet) at 2.0 mm. The <2.0 mm material was passed over a shaking table to pre-concentrate heavy minerals. Visible gold grains were counted and a visible gold assay was calculated. The <2.0 mm material was then sieved (dry) to 0.25 mm. The heavy mineral pre-concentrate was separated using a liquid with a specific gravity of 3.0 to recover indicator minerals. Ferromagnetic heavy minerals were separated from the HMC using a magnet and sieved (dry) to produce four fractions (<0.25 mm, 0.25-0.5 mm, 0.5-1.0 mm, 1.0-2.0 mm). The non-ferromagnetic fraction of heavy minerals was sieved (dry) to produce four fractions with the same grain-size intervals as the ferromagnetic fraction. The 0.25 to 0.5 mm, 0.5 to 1.0 mm, and 1.0 mm to 2.0 mm ferromagnetic and non-ferromagnetic fractions were randomly split into sub-samples at Université Laval, Québec. Following the procedure described in Sappin et al. (2014), ~100 grains from the ferromagnetic fraction of each sample were mounted in epoxy sections and polished for chemical analysis by Electron Probe Micro-Analysis (EPMA). Tourmaline grains were handpicked from the 0.25 to 0.5 mm fraction under a binocular microscope; scheelite grains were identified using a UV light. Tourmaline, scheelite and magnetite grains were mounted in epoxy sections and polished for chemical analysis by EPMA and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS).

3.3 Analytical methods

3.3.1 Electron probe micro-analysis

Major and minor elements in tourmaline, scheelite, and magnetite were analyzed with a CAMECA SX-100 electron probe equipped with five WDS spectrometers at the Université Laval, Québec (Supp. Material 1). Major elements were analyzed in tourmaline (Fe, Cr, Ca, Na, Mg, Si, and Al) and scheelite (Ca and W) using a 10 µm beam, 15 kV voltage and 20 nA current, counting 10 s on both sides for background and 20 s at peak. Minor elements were analyzed in tourmaline (Mn, Ti, Zn, Cu, Ni, Co, V, Sc, K, Cl, Sr, and F) and scheelite (Fe, Sr, Mo, Na, and Y), using a 10 µm beam, 15-25 kV voltage and 100 nA current, counting 15-30 s on background and 40-120 s at peak. Tourmaline data were normalized to 29 oxygens and the structural formula was calculated using an Excel spreadsheet from Henry et al. (2011), assuming stoichiometric values for B (3 apfu) and OH (4 apfu; except if F and/or Cl were measured by EPMA). Magnetite was analyzed for minor elements (V, Cr, Zn, Cu, Ni, Mn, K,
Sn, Ca, Ti, Al, Si and Mg), using a 10 µm beam, 15 kV voltage, and 100 nA current, counting 15-20 s on both sides for background and 40-80 s at peak, which is similar to analytical conditions described in Dupuis and Beaudoin (2011), Boutroy et al. (2014), and Makvandi et al. (2016a). Calibration of the instrument was achieved using both natural and synthetic standards. The range of detection limits for each element is reported in Supp. Material 1.

3.3.2 Laser ablation-inductively coupled plasma-mass spectrometry

Trace elements in tourmaline and scheelite were analyzed with a RESOlution M-50 Excimer 193 nm laser coupled to an Agilent 7700x ICP-MS at the Laboratoire des Matériaux Terrestres (LabMaTer) of Université du Québec à Chicoutimi (Supp. Material 2). Tourmaline was analyzed by ablating linear trenches in order to determine the concentration of $^7$Li, $^9$Be, $^{23}$Na, $^{25}$Mg, $^{27}$Al, $^{39}$K, $^{43}$Ca, $^{45}$Sc, $^{47}$Ti, $^{51}$V, $^{53}$Cr, $^{55}$Mn, $^{57}$Fe, $^{59}$Co, $^{60}$Ni, $^{65}$Cu, $^{66}$Zn, $^{71}$Ga, $^{85}$Rb, $^{86}$Sr, $^{89}$Y, $^{92}$Zr, $^{93}$Nb, $^{95}$Mo, $^{118}$Sn, $^{133}$Cs, $^{139}$La, $^{140}$Ce, $^{141}$Pr, $^{146}$Nd, $^{152}$Sm, $^{153}$Eu, $^{155}$Gd, $^{159}$Tb, $^{163}$Dy, $^{165}$Ho, $^{166}$Er, $^{169}$Tm, $^{172}$Yb, $^{175}$Lu, $^{179}$Hf, $^{181}$Ta, $^{207}$Pb, $^{232}$Th, and $^{238}$U in the core and rim of the grains. LA-ICP-MS analysis used a beam size of 33 to 44 µm, a laser frequency of 10-15 Hz, and a speed stage of 5 µm/s. Calibration was completed using NIST SRM 610, GSD, and GSE as external standards, with Si (determined by EPMA) as an internal standard. Reference materials NIST SRM 612, GSD, and GSE were used to monitor the quality of analyses. Scheelite was analyzed by ablating linear trenches in order to determine the concentration of $^7$Li, $^{11}$B, $^{23}$Na, $^{24}$Mg, $^{29}$Si, $^{39}$K, $^{43}$Ca, $^{45}$Sc, $^{47}$Ti, $^{51}$V, $^{53}$Cr, $^{55}$Mn, $^{57}$Fe, $^{59}$Co, $^{65}$Cu, $^{66}$Zn, $^{75}$As, $^{86}$Sr, $^{89}$Y, $^{92}$Zr, $^{93}$Nb, $^{95}$Mo, $^{107}$Ag, $^{118}$Sn, $^{137}$Ba, $^{139}$La, $^{140}$Ce, $^{146}$Nd, $^{147}$Sm, $^{153}$Eu, $^{157}$Gd, $^{159}$Tb, $^{163}$Dy, $^{165}$Ho, $^{166}$Er, $^{169}$Tm, $^{172}$Yb, $^{175}$Lu, $^{181}$Ta, $^{182}$W, $^{207}$Pb, $^{232}$Th, and $^{238}$U. LA-ICP-MS analysis used a beam size of 44 µm, a laser frequency of 10-15 Hz, and a speed stage of 5-20 µm/s. Calibration was completed using NIST SRM 610, GSD, and GSE as external standards, with Ca (determined by EPMA) as an internal standard. Reference materials NIST SRM 612, GSD, and GSE were used to monitor the quality of analyses. Data reduction was completed using the Iolite software (Paton et al. 2011). The range of detection limits for each element is reported in Supp. Material 2.

3.4 Statistical methods

Data measured by EPMA or LA-ICP-MS are labeled censored data when their value is below the respective limit of detection (Helsel 2005). A number of methods exist to process these censored data, such as the exclusion of values or arbitrary substitutions. In this study, the data were imputed using the imputation of k-nearest neighbors as described in Makvandi et al. (2016). The data were also transformed to centered log-ratio to overcome the effects of closure (Makvandi et al. 2016). Centered log-ratio transformation is symmetric with an orthonormal basis and is recommended for multivariate statistical techniques like PCA. Our transformed results were then analyzed using PCA, following Makvandi et al. (2016), in order to investigate the complex variance in compositional data by sorting out discriminator elements that differentiate the geological samples based on chemical composition.
4. Petrography

4.1 Quartz veins

Tourmaline in the Val-d’Or district is a common mineral in subvertical veins in shear zones and in subhorizontal veins in extensional fractures between shear zones. In fault-fill veins, tourmaline typically forms parallel ribbons defined as a “slip surface” that developed during shearing, whereas in extensional veins tourmaline is distributed close to the walls of the ribbons where they typically form rosettes of needles (Robert and Brown 1986b). The average volume proportion of tourmaline in gold-bearing quartz veins of the district ranges between 10 and 15%, with some veins locally containing up to 90%, but tourmaline is quite rare at the Lapa and Kiena deposits. In macroscopic observation, tourmaline is black (Fig. 3A). In thin section, blue cores and brown rims are characteristic (Fig. 3B). Lapa and Orenada tourmalines have a lighter brown rim, whereas Sigma 2 tourmaline displays a darker brown rim, which differentiates these from most tourmalines of the Val-d’Or district. Tourmaline also shows complex sector zoning (Fig. 3B), irregular patchy zoning (Fig. 3D), and more rarely oscillatory zoning (Fig. 3C). Typical are euhedral, fine- to coarse-grained acicular crystals, rarely exceeding 0.5 mm in diameter. Coarse tourmaline grains tend to occur as isolated needles surrounded by quartz (Fig. 3A), whereas smaller tourmaline needles commonly form massive and irregular aggregates within the quartz veins (Fig. 3A). Tourmaline also forms rosettes, poikilitic grains with inclusions of calcite and quartz within the tourmaline crystal (Fig. 3E) and may be aligned parallel to each other forming fibrous masses.

Scheelite is an accessory mineral in gold-bearing quartz veins of the Val-d’Or district. Scheelite is characterized by a beige color and form centimeter-sized aggregates of massive euhedral to anhedral grains (Figs. 3G, H, I). Cathodoluminescence combined with backscattered electron imaging show no zonation in scheelite. Most scheelite crystals are fractured and filled with quartz and/or carbonate. Tourmaline needles, quartz, and idioblastic pyrite may be juxtaposed to the scheelite crystals.

Magnetite is rare in gold-bearing quartz veins of the Val-d’Or district, but is common within the intrusive host rocks. Hydrothermal magnetite occurs as finely disseminated euhedral to anhedral (up to 0.05 mm) inclusions in pyrite (Fig. 3J) or near pyrite within the quartz veins, whereas magmatic magnetite (Fig. 3D) forms larger euhedral crystals (up to 0.5 mm) in these host rocks. Some magmatic magnetite grains have a chromite core (Fig. 3D).

4.2 Till samples

Gold grains were found in all glacial sediment samples in which the largest gold grain is 0.25 mm in length. The number of gold grains normalized to 10 kg samples increases from 9 in the up-ice sample (14-DG-001) to 61
in the northernmost sample (14-DG-002) within the Val-d’Or district (Fig. 2A). Samples 14-DG-005, 14-DG-004, and 14-DG-003 contain, respectively, 9, 40, and 4 gold grains (Fig. 2A), indicating a diminution of gold grain counts in till samples located down-ice of sample 14-DG-002. Gold grains recovered from samples 14-DG-002 and 14-DG-004 within the district show pristine, modified, and reshaped forms, whereas samples 14-DG-001, 14-DG-005, and 14-DG-003 contain reshaped grains only. The presence of pristine grains in samples 14-DG-002 \( (n = 16) \) and 14-DG-004 \( (n = 10) \) suggests a proximity to bedrock gold deposits. However, the pristine form of a gold grain recovered in till may result from the disaggregation of a polymineralic grain containing gold, which retains the pristine form of a gold grain on a longer transport distance, thus making the argument of proximity questionable. Till sample 14-DG-005 was collected just south of bedrock gold deposits and contains only reshaped gold grains.

Tourmaline grains were retrieved from the 0.25 to 0.5 mm size fraction of the HMC from all glacial sediment samples. No tourmaline grain was recovered from the size fractions larger than 0.5 mm. Within the Val-d’Or district, the number of tourmaline grains normalized to 10 kg samples increases from 26 in the up-ice sample (14-DG-001) to 56 in the northernmost sample (14-DG-002), before gradually decreasing to 14 in the down-ice sample (14-DG-003) located south of the district (Fig. 2B). Samples 14-DG-002, 14-DG-005, and 14-DG-004, from within the limits of the Val-d’Or district, contain more tourmaline grains compared to the northern- and southern-most samples. Grains recovered in the glacial sediment samples are characteristically black (Fig. 3F). Most tourmaline grains occur as euhedral needles, broken perpendicular to the c-axis, corresponding to the primary texture of tourmalines associated with the gold mineralization. Aggregates of tourmaline needles and quartz were also recovered in till samples. In backscattered electron images, tourmaline grains from till lack zonation. The petrographic characteristics of tourmaline grains recovered in glacial sediment samples are similar to those of tourmalines observed in the gold-bearing quartz veins.

Scheelite grains were recovered from the 0.25 to 0.5 mm size fraction of the HMC of glacial sediment samples 14-DG-002 \( (n = 2) \) and 14-DG-003 \( (n = 1) \; (Fig. 2B) \). No scheelite was found in samples 14-DG-001, 14-DG-004, and 14-DG-005. The three scheelite grains recovered in the glacial sediments occur as beige, subhedral to anhedral grains lacking zonation. Petrographic features of these grains are similar to those observed in scheelite from gold-bearing quartz veins.

Magnetite grains were retrieved from the 0.5 to 2.0 mm ferromagnetic size fraction of the HMC from all glacial sediment samples. Magnetite is the dominant mineral in the ferromagnetic fraction and constitutes 65 to 78% of the fraction (Fig. 2C). Other minerals such as hematite, titanomagnetite, ilmenite, and chromite were also recovered from the ferromagnetite fraction (Fig. 2C). Magnetite grains recovered in the glacial sediment samples occur as finely disseminated grains in a mineral aggregate (Fig. 3L), or as large monomineralic grains. In backscattered electron images, magnetite grains from till lack zonation.
5. Geochemistry

5.1 Tourmaline

5.1.1 Quartz veins

Tourmaline from gold-bearing quartz veins of the Val-d’Or district belongs to the alkali group (Fig. 4A) and shows a dravite-schorl composition (Fig. 4C; Henry et al. 2011). Type I and III tourmalines are characterized by Mg/(Mg+Fe) ratios between 0.51 and 0.79 and plot, exclusively, within the dravite field (Fig. 4C). Type I tourmaline from the Goldex, Triangle Zone, and Audet deposits tends to be Mg-rich with Mg/(Mg+Fe) between 0.62 and 0.79, and a Mg content reaching 2.27 apfu. In contrast, Type II tourmaline has a variable Mg/(Mg+Fe) ratio between 0.32 and 0.63, and plots in both the schorl and dravite fields (Fig. 4C). Most tourmalines from the Sigma 2, Bloc Sud, Lac Simon, and Paramaque deposits are schorl with a lower Mg/(Mg+Fe) of 0.32 to 0.53, whereas most tourmalines from the Siscoe and Brosnor deposits have a dravite composition with higher Mg/(Mg+Fe) ranging from 0.47 to 0.63. Type I, II, and III tourmalines have similar Al contents with an average of 6.16, 6.02, and 6.27 apfu, respectively. Average Fe$_{tot}$+Mg contents are 2.77 (I), 2.85 (II), and 2.67 (III) apfu, respectively, which indicates that the Z-site is generally occupied by 6 Al cations, with substantial Al present in the Y-site due to alkali defect and/or dehydroxylation-type substitutions. The Si contents in the T-site are similar for types I, II, and III tourmalines with an average of 5.96, 6.00, and 5.97 apfu, respectively. Type I, II, and III tourmalines have average Na contents of 0.70, 0.73, and 0.69 apfu, respectively, and low Ca contents averaging 0.09, 0.06, and 0.05 apfu, respectively, and low X-site vacancies of 0.22, 0.21, and 0.26 apfu, respectively. Type I, II, and III tourmalines show negligible F (up to 0.25 apfu) and Cl (up to 0.01 apfu) contents.

Concentrations of trace elements in tourmaline display significant variations over several orders of magnitude. Minor elements such as K, Sc, Ti, V, Cr, Mn, Ni, Zn, Ga, and Sr have averages of tens to hundreds of ppm, with Ti being the most abundant minor element reaching an average concentration of a few thousands of ppm. Average contents of trace elements such as Li, Be, Co, Cu, Rb, Y, Zr, Nb, Mo, Sn, Cs, Ba, REE, Hf, Ta, Pb, Th, and U rarely exceed 10 ppm with the lowest concentrations typically below the detection limit. Type I, II, and III tourmalines have uniformly low contents of, and lack significant variations for, Be, Y, Mo, REE, high field strength elements such as Zr, Nb, Hf, Th, U, and Ta, and large ion lithophile elements such as Rb, Cs, and Ba.

The average concentration of trace elements in tourmaline show some systematic variations according to deposit setting (Fig. 5). In general, Type I tourmaline hosted in calc-alkaline intrusions of felsic to intermediate composition generally has lower concentrations of Sc, V, Cr, Co, Ni, and Sn, but similar K, Mn, Cu, Zn, Ga, and Pb contents to Type II tourmaline hosted in mafic rocks of tholeiitic affinity. Lithium, K, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Sr, Sn, and Pb show the largest compositional variations in tourmaline from orogenic gold deposits of the Val-d’Or district.
Two distinct chondrite-normalized REE patterns (Fig. 6) are distinguished for tourmaline from the Val-
d’Or district: (1) flat LREE showing an enrichment in HREE with a positive Eu anomaly (Pattern A; Fig. 6A), and (2) flat HREE showing a slight enrichment of LREE with a positive Eu anomaly (Pattern B; Fig. 6B). Tourmaline generally displays both REE patterns within a single grain, which correlates with concentric zoning. For example, the core of the tourmaline grain of sample 96-DP-162 is characterized by REE pattern A, whereas the rim has REE pattern B (Figs. 6C, D). However, some tourmalines show only one of the two REE patterns despite the presence of zonations. Tourmaline with higher $\Sigma$REE is generally characterized by higher Y and Zr contents.

5.1.2 Till samples

Tourmaline from till samples of the Val-d’Or district also belongs to the alkali group (Fig. 4B) and shows a dravite-schorl composition (Fig. 4D; Henry et al. 2011). Till tourmaline is characterized by a Mg/(Mg+Fe) ratio between 0.27 and 0.78. The same two distinct chondrite-normalized REE patterns (Fig. 6) are distinguished for till tourmaline from the district: (1) flat LREE showing an enrichment in HREE with a positive Eu anomaly (Pattern A; Fig. 6E), and (2) flat HREE showing a slight enrichment of LREE with a positive Eu anomaly (Pattern B; Fig. 6F).

5.2 Scheelite

5.2.1 Quartz veins

Scheelite from gold-bearing quartz veins and till samples of the Val-d’Or district show a narrow range in composition. Hexavalent Mo can substitute for W$^{6+}$, forming a complete solid solution series between scheelite (CaWO$_4$) and powellite (CaMoO$_4$). Scheelite is characterized by similar major element contents, where Ca and W range from 13.76 to 14.08 wt% and 62.01 to 64.29 wt%, respectively, and Mo is lower than 0.02 wt%. Because the Mo content in scheelite from the Val-d’Or district is low, Mo is considered here a trace element.

Trace elements in scheelite range over a few orders of magnitude for Na, K, Fe, S, Sr, Y, Mo, Pb, and most REE with average concentrations ranging from tens to hundreds of ppm. Average contents of Li, B, Mg, Si, Ti, V, Cr, Mn, Co, Cu, Zn, As, Nb, Ag, Sn, Ba, Tm, Lu, Ta, Th, and U rarely exceed 10 ppm with the lowest concentrations typically below detection limit. Scheelite from the Val-d’Or district lacks significant variation in concentration for several trace elements including Li, B, Ti, Co, Ba, Ta, Th and U; most Si, Cr, Ag, and Sn analyses in scheelite are below detection limit. Magnesium, S, K, V, Mn, Cu, Zn, As, Sr, Nb, Mo, and Pb show the largest compositional variations, whereas Na, Fe, and Y display significant variation but are not characteristic elements in scheelite from the Sigma, Beaufor, and Triangle Zone deposits.
Scheelite from the gold-bearing quartz veins is characterized by distinctive bell-shaped REE patterns with either a positive or negative Eu anomaly (Fig. 7). Samples from the Sigma deposit have a positive Eu anomaly (Eu/Eu* = 1.95-5.10) and a maximum enrichment centered between Sm and Gd (Fig. 7A). Sigma scheelite is characterized by high \( \Sigma \)REE with an average of 1118 ppm (649-1567 ppm), and relatively high \((\text{La}/\text{Sm})_N\) and low \((\text{Gd}/\text{Lu})_N\) ratios ranging from 0.09 to 0.34 and 3.32 to 9.57, respectively. Scheelite from the Sigma deposit is enriched in LREE \((\text{La}/\text{Lu})_N = 0.5-1.58\) compared to samples from the Beaufor and the Triangle Zone \((\text{La}/\text{Lu})_N = 0.17-1.02\). Scheelite from these two deposits is characterized by relatively low \((\text{La}/\text{Sm})_N\) and high \((\text{Gd}/\text{Lu})_N\) ratios ranging from 0.01 to 0.04 and 16.27 to 36.04, respectively, and bell-shaped REE patterns with a small negative Eu anomaly (Figs. 7B, C; Eu/Eu* = 0.52-0.83). Beaufor and Triangle Zone scheelite has high \( \Sigma \)REE with averages of 1192 ppm and 1685 ppm, respectively. The sum of the REE ranges from 412 to 2070 ppm in scheelite from Beaufor and from 1259 to 2068 ppm in scheelite from Triangle Zone.

5.2.2 Till samples

Scheelite grains from glacial sediment samples have major element contents of 13.82 to 13.97 wt.% Ca and 64.60 to 68.60 wt.% W. Two till scheelite grains are characterized by REE patterns similar to those from the Beaufor and Triangle Zone deposits (Fig. 7D). These grains display bell-shaped REE patterns with either a small or large negative Eu anomaly (Figs. 7D; Eu/Eu* = 0.42-0.94), and by lower \( \Sigma \)REE (avg 588 ppm), similar to the low \( \Sigma \)REE samples from the Beaufor deposit. One till scheelite grain displays a profile with a negative Eu anomaly and normalized REE values that consistently lie below 100. This profile represents an unknown source. We did not retrieve scheelite grains from till with the REE pattern of scheelite from the Sigma deposit. The till scheelite also has relatively low \((\text{La}/\text{Sm})_N\) and medium to high \((\text{Gd}/\text{Lu})_N\) ratios ranging from 0.08 to 1.37 and 6.20 to 10.67, respectively.

5.3 Magnetite

5.3.1 Quartz veins

Trace elements in magnetite and hematite from gold-bearing quartz veins and their host rocks show significant compositional variations, ranging over a few orders of magnitude for Mg (25-7405 ppm), Al (32-8017 ppm), Si (26-9927 ppm), P (3-73 ppm), K (18-274 ppm), Ca (21-20181 ppm), Ti (20-17989 ppm), V (56-7447 ppm), Cr (10-32409 ppm), Mn (20-1876 ppm), Ni (20-2340 ppm), Cu (97-560 ppm), Zn (127-1010 ppm), and Sn (54-240 ppm). Hydrothermal magnetite from the Goldex, Sigma, and Louvicourt deposits and hydrothermal hematite from the Vein No. 5 and Lac Herbin deposits is characterized by higher Cr, Zn, Mn, K, Ca, Ti, and Al than
magnetic magnetite from the Beaufor and Bloc Sud intrusive host rocks. Magnetite from the Louvicourt deposit shows a relatively high Ni content, whereas hematite from the Vein No. 5 deposit shows a high Sn content.

Several compositional diagrams have been proposed by Dupuis and Beaudoin (2011) to discriminate magnetite from diverse ore deposits and rock types. The Ni+Cr vs Si+Mg diagram is used to identify magnetite from Ni-Cu-PGE deposits. Data for magnetite from gold-bearing quartz veins and from the intrusive host rocks of the Val d’Or district plot outside the field defined by Ni-Cu-PGE magnetite on this diagram (Fig. 8A) with the exception of data for three magnetite grains from the Louvicourt deposit. Magnetite data from the district plot in various fields including those for skarn, porphyry, Kiruna, and Fe-Ti and V deposits on the Ca+Al+Mn vs Ti+V diagram (Fig. 8C). However, most hydrothermal magnetite and hematite can be discriminated from magmatic magnetite in the Ca+Al+Mn vs Ti+V diagram. Data for hydrothermal magnetite from the Goldex and Sigma deposits and hydrothermal hematite from the Lac Herbin and Vein No. 5 deposits plot in the upper part of the diagram with the exception of Louvicourt magnetite. Magmatic magnetite from the Beaufor and Bloc Sud intrusive host rocks plots in the lower part of the diagram in an undefined field, which is below the field defined by BIF, IOCG, and Kiruna magnetite.

5.3.2 Till samples

In the Ni+Cr vs Si+Mg diagram, data for most till magnetite plot outside the field defined by Ni-Cu-PGE magnetite with the exception of a few grains (Fig. 8B). Till magnetite plots in every field defined in the Ca+Al+Mn vs Ti+V diagram (Fig. 8D). Several magnetite grains recovered in till sample 14-DG-002 show a chemical signature similar to that of magmatic magnetite from the host rocks of the Beaufor and Bloc Sud deposits. In contrast, magnetite from till samples 14-DG-001, 14-DG-003, 14-DG-004, and 14-DG-005 lacks this chemical signature.

6. Principal component analysis

Conventional data presentation methods such as binary and ternary diagrams are useful for datasets where a limited number of variables can be selected to show variation between and among samples. In contrast, multivariate statistical methods such as PCA allow the investigation and characterization of the complex chemical signatures of tourmaline and scheelite from the Val-d’Or district by considering a wide array of major, minor, and trace elements, resulting in better sample classification and discrimination.

6.1 Quartz veins

6.1.1 Tourmaline
The PCA of LA-ICP-MS data comprises more elements than that from the EPMA analyses, allowing better chemical discrimination of tourmaline from orogenic gold deposits of the Val-d’Or district. However, because of the small grain size, no tourmaline from the Audet, Canmet (nord), Lac Simon, Nord-Ouest, Orenada, Siscoe, and Snowbank deposits was analyzed by LA-ICP-MS. Figure 9 shows the PCA results, which are defined by the combination of correlations among several elements including Li, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Nb, Sn, Ba, La, Eu, Lu, and Pb. In this analysis, PC1, PC2, and PC3 contribute, respectively, 17.6%, 16.4%, and 16.0% of the total variance, for a total of 50.0%. PC1 is defined by high contributions of Al, Na, Mg, Ga, Zn, Fe, Mn, and Ca, whereas PC2 is defined by high contributions of Nb, Sn, Mn, Li, Fe, and Co, and PC3 is defined by high contributions of Ti, Eu, La, Ca, Sr, Ba, Pb, Nb, and Mn. On the PC1-PC2 projection (Fig. 9A), Type I tourmaline forms a large cluster in the middle of the plot. Type II tourmaline from Brosnor and Bloc Sud form a cluster with negative PC1, whereas Sigma 2 and Paramaque Type II tourmaline forms a cluster with positive PC2, slightly overlaping with Lac Herbin tourmaline. Type III tourmaline from the Lapa deposit defines a small cluster in the upper-left quadrant, overlapping with Type I tourmaline.

In addition to classifying tourmaline from gold mineralization of the Val-d’Or district, PCA is useful for comparing tourmaline chemistry from orogenic gold deposits elsewhere (this study; Deksissa and Koeberl 2002; Jiang et al. 2002; Hazarika et al. 2015, 2016) and from various deposit types such as vein-type Pb-Zn-Cu±U (Yavuz et al. 2011), Cu-Mo porphyry (Iveson et al. 2016), vein-type Sn (Jiang et al. 2004), emerald (Galbraith et al. 2009), massive sulfide (Griffin et al. 1996; Slack et al. 1999), tourmalinite (Griffin et al. 1996), and from pegmatitic and hydrothermal systems of the Schwarzwald area in Germany (Marks et al. 2013). Because different trace element suites are reported, two PCA models had to be constructed using 17 trace elements (La, Ce, Nd, Sm, Eu, Yb, Lu, Sc, Ti, V, Zn, Sr, Y, Zr, Ba, Pb, and Cr; Fig. 10) and 16 major and trace elements (Ti, Al, Fe, Mn, Mg, Ca, Na, K, Zn, Cu, Sr, Zr, Sn, Ba, Pb, and Cr; Fig. 11).

Figure 10 shows the PCA results of tourmaline data from orogenic gold (Val-d’Or, Big Bell, Mount Gibson, Hutti, Uti, Hira-Buddini, Okote), vein-type Sn (Yunlong), Cu-Mo porphyry (Margaret), and vein-type Pb-Zn-Cu±U (Asarcık) deposits. In this analysis, PC1, PC2, and PC3 contribute, respectively, 33.1%, 15.3%, and 9.6% of the variance, for a total of 58.0%. PC1 is defined by high contributions of Sc, V, Zn, Sr, Ti, Cr, and Eu in decreasing order of importance. PC2 is defined by high Yb, Lu, Zr, Cr, and Y, whereas PC3 is defined by high contributions of Pb, Ba, Sr, Yb, Lu, and Zn. Tourmaline from orogenic gold deposits defines a large cluster in the middle of the PC1-PC2 projection (Fig. 10A), whereas tourmaline data from the Yunlong, Margaret, and Asarcık deposits form a cluster with negative PC1, slightly overlapping the field for orogenic gold deposits tourmaline.

Figure 11 shows the PCA results of tourmaline from orogenic gold (Val-d’Or), massive sulfide (e.g., Kidd Creek, Sullivan), tourmalinite, and emerald (Tsa de Glisza) deposits, and from the pegmatitic and hydrothermal systems of the Schwarzwald area. In this analysis, PC1, PC2, and PC3 contribute, respectively, 35.8%, 19.2%, and
8.0% of the variance, for a total of 63.0%. PC1 is defined by high contributions of Na, Al, Fe, Mg, Ca, Sr, and K in decreasing order of importance. PC2 has high contributions of Mn, Zn, Sn, and K, whereas PC3 is defined by high contributions of Pb, Ca, Mn, and Sn. The PC1-PC2 projection (Fig. 11A) shows that orogenic gold deposit tourmaline forms a large cluster with positive PC1, whereas tourmaline data from massive sulfide, tourmalinite, and emerald deposits have negative PC1. Massive sulfide and tourmalinite tourmalines show the highest negative values along PC1, and form overlapping clusters. Tourmaline from the Tsa de Glisza emerald deposit forms a cluster between orogenic gold and massive sulfide/tourmalinite fields. Tourmaline from the pegmatitic-hydrothermal system of the Schwarzwald area has positive PC2, with pegmatitic tourmaline showing the highest positive score.

6.1.2 Scheelite

The following elements, measured by LA-ICP-MS, are used in the PCA: Li, B, Na, Mg, S, K, Ti, V, Mn, Fe, Co, Cu, Zn, As, Sr, Y, Nb, Mo, Ba, La, Eu, Lu, Ta, Pb, Th, and U. The PCA results are shown in scatter plots PC1-PC2 (Fig. 12). In this analysis, PC1, PC2, and PC3 contribute, respectively, 33.2%, 22.0%, and 10.0% of the variance, for a total of 65.2%. PC1 is defined by high contributions of Eu, Lu, La, S, Y, Na, and Pb in decreasing order of importance. PC2 has high contributions of Nb, Ta, Y, Sr, Na, Li, and Mn, whereas PC3 is defined by high contributions of B, Fe, Ti, Mn, and Li. Scheelite forms three distinct clusters on the PC1-PC2 projection, corresponding to each deposit (Sigma, Beaufor, and Triangle Zone of the Lamaque Sud gold project). Triangle Zone and most Beaufor deposits scheelites plot with negative PC1, whereas scheelite from the Sigma deposit has positive PC1. Beaufor scheelite plots on the positive side of PC2 while scheelite from the Triangle Zone plots with negative PC2.

In addition to classifying scheelite from orogenic gold deposits of the Val-d’Or district, PCA is used to compare scheelite chemistry from various orogenic gold deposits (this study; Hazarika et al. 2016; Sciuba et al. submitted) and from W-Mo skarn deposits of the Chizhou area (Song et al. 2014). Because different trace-element suites are available in the literature for scheelite, two PCA models were defined, one using 24 elements (B, Na, Mg, S, K, Ti, V, Mn, Fe, Co, Cu, Zn, As, Sr, Y, Nb, Mo, Ba, Ta, Pb, Th, U, Eu*, and ΣREE; Fig. 13) and the second using 19 elements (Sr, Y, Mo, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Pb; Fig. 14).

Figure 13 shows the PCA results of scheelite data from orogenic gold deposits including Val-d’Or (this study), Essakane, Macraes, Canadian Malartic, Kumtor, Buzwagi, Young Davidson, Cuiaba, Edward’s Find, Hutti, Meliadine, Mt Charlotte, Mt Pleasant, Dome, Norseman, Nevoria, Paddington, Marvel Loch, Tarmoola, and Kochkar (Sciuba et al. submitted). In this analysis, PC1, PC2, and PC3 contribute, respectively, 20.4%, 14.1%, and 10.2% of the variance, for a total of 44.7%. PC1 is defined by high contributions of Nb, ΣREE, Y, As, Ta, V, Na, and Mo in decreasing order of importance. PC2 has high contributions of K, Na, Zn, Cu, Pb, ΣREE, B, Y, and Eu*,
whereas PC3 is defined by high contributions of Mn, Eu*, S, Ta, Zn, K and Nb. On the PC1-PC2 projection, scheelite from deposits hosted by felsic to intermediate rocks (Sigma, Beaufor, Triangle Zone, and Young Davidson), with the exception of the Kochkar deposit, and scheelite from sediment-hosted deposits (Essakane, Malartic, Macraes) form two distinct clusters in opposite quadrant indicating that they have opposite features. Scheelite in mafic- to ultramafic-hosted deposits (Cuiaba, Edwar’s Find, Hutti, Mt Charlotte, Mt Pleasant, Dome, Norseman, Nevoria, Paddington, Marvel Loch, Tarmoola) form a cluster extending from the upper-left quadrant to the lower-right quadrant.

Figure 14 shows the PCA result for scheelite data from orogenic gold deposits including Val-d’Or (this study), Hutti (Hazarika et al. 2016), and elsewhere (Sciub et al. submitted), and from W-Mo skarn deposits from the Chizhou area (Song et al. 2014). In this analysis, PC1, PC2, and PC3 contribute, respectively, 58.3%, 18.6%, and 11.2% of the variance, for a total of 88.1%. PC1 is defined by high contributions of Y and HREE, whereas PC2 has high contributions of MREE with the exception of Eu. PC3 is defined by high contributions of Eu, Pb, and Sr. The PC1-PC2 projection shows that most orogenic gold deposit scheelites form a large cluster in the middle of the plot, with scheelite from the Sigma, Beaufor, and Triangle Zone deposits (this study) having higher positive PC1 and PC2 scores. Scheelite from the Crusader deposit defines a distinct cluster in the lower-right quadrant of the scatter plot, whereas W-Mo skarns scheelite (Chizhou area) form a distinct cluster on the negative side of PC1.

6.2 Till samples

6.2.1 Tourmaline

In order to determine the provenance of tourmaline grains recovered in glacial sediment samples, LA-ICP-MS till data have been projected on PCA models defined by tourmaline associated with gold mineralization (Fig. 9). PCA results show that most grains plot in the field defined by Type I tourmaline (Fig. 9B) with two tourmaline grains plotting in the field defined by Type II tourmaline. In Figure 9B, data for two tourmaline grains plot in the field defined by tourmaline from the Brosnor and Bloc Sud deposits; no tourmaline plots in the field defined by the Sigma 2 and Paramaque deposits. The Sigma 2, Brosnor, and Bloc Sud deposits are, respectively, located 8, 12, and 14 km east of the till sample transect, such that tourmaline from those deposits could not be incorporated in the till samples because they are not along the ice-flow path. The only deposit containing Type II tourmaline, located along the transect, is Paramaque, 0.75 km up-ice of till sample 14-DG-004. This relationship suggests that some tourmaline grains from till samples 14-DG-004 and 14-DG-005 should plot in the field defined by Type II tourmaline, which is not the case (Fig. 11B). However, several till tourmaline grains from these samples were not analyzed by LA-ICP-MS owing to their small size.
Chemical data for till tourmaline of the Val-d’Or district have been projected on both PCA defined by tourmaline from various deposit types (Fig. 10, 11). Most till data plot in the field defined by tourmaline from orogenic gold deposits (Fig. 10B; Fig. 11B) with results for a few grains falling outside but close to the boundary of the orogenic gold tourmaline field.

### 6.2.2 Scheelite

LA-ICP-MS chemical data for 3 scheelite grains recovered in glacial sediments were projected on PC1-PC2 (Fig. 12B) to constrain their provenance. Data for two scheelite grains from till samples 14-DG-002 and 14-DG-003 plot close to the field defined by scheelite from the Beaufor deposit, whereas results from the other scheelite grain in sample 14-DG-002 plot close to the field defined by scheelite from the Triangle Zone deposit. In Figure 12B, scheelite grains from till samples 14-DG-002 and 14-DG-003 plot, respectively, in or close to the field defined by scheelite from the Beaufor deposit, which is located less than 1 km up-ice from till sample 14-DG-002. No till scheelite data plot in the field defined by Sigma and Triangle Zone scheelite. The Sigma deposit and Triangle Zone are located 14 km west of the till sampling transect, which suggests that scheelite from those deposits should not be recovered from the till samples.

Chemical data for till scheelite of the Val-d’Or district have been projected on both PCA models defined by scheelite from various deposit types (Figs. 13, 14). In Figure 13B, data for two scheelite grains from till samples 14-DG-002 and 14-DG-003 plot in or close to the field defined by scheelite from the district and show a chemical signature similar to scheelite from the Beaufor deposit. The other scheelite grain, from till sample 14-DG-002, has a chemical signature similar to scheelite from the Canadian Malartic deposit, which is located 40 km west of the till sampling transect. In Figure 14B, scheelite grains from till samples 14-DG-002 and 14-DG-003 plot, respectively, in and close to the field defined by scheelite from orogenic gold deposits of the Val-d’Or district.

### 7. Discussion

#### 7.1 Causes of compositional variations in tourmaline

Robert and Brown (1986b) proposed a vein paragenesis for the gold-bearing veins of the Sigma deposit in which Ca-bearing minerals (e.g., carbonate, scheelite, apatite, epidote) are the first to precipitate, followed by crystallization of tourmaline and pyrite. Mass-balance calculations show that during filling of the veins, hydrothermal fluids contributed Ca, Na, Si, CO₂, B, S, and P to precipitated minerals, whereas Mg, Fe, Al, and Ti were derived from the breakdown of wall rock chlorite and biotite (Robert and Brown 1986b). Calcium from the hydrothermal fluid was incorporated in Ca-bearing minerals, resulting in low Ca/(Ca+Na) ratios in tourmaline from orogenic gold deposits of the Val-d’Or district. The release of Mg, Fe, Ti, and Al caused by fluid-rock interaction
favored the deposition of tourmaline and pyrite in the veins and wall rocks. Mg-rich tourmaline hosted in tholeiitic igneous rocks may result from partitioning of Fe into co-precipitating Fe-sulfides (Henry and Dutrow 1993; Slack 1996; Jiang et al. 2002), or from high fluid/rock ratios wherein tourmaline chemistry reflects preferentially the composition of the fluid with minor chemical control by the host rock (Jiang et al. 2002). Because tourmaline and Fe-sulfides co-precipitated during vein formation, Fe partitioning into pyrite, pyrrhotite, and/or arsenopyrite, resulted in Fe depletion of tourmaline. Tourmaline that lacks an association with Fe-sulfides generally shows a higher Fe content. Alternatively, the hydrothermal alteration of the high Mg host rocks, during which chlorite was destroyed, contributed to the high Mg/(Mg+Fe) ratio in tourmaline.

Type I tourmaline occurs in gold-bearing quartz veins containing pyrite. Because Fe is preferentially partitioned into pyrite, Type I tourmaline is characterized by a low Fe content in the Y-site and Mg/(Mg+Fe) ratio above 0.5, which together with low vacancies in the X-site suggest a dravitic composition (Fig. 4C). Type I tourmaline from the Goldex, Triangle Zone, and Audet deposits has a high pyrite content yielding a lower Fe content than most Type I tourmaline and thus, a higher Mg/(Mg+Fe) ratio up to 0.79. Type II tourmaline from the Sigma 2, Bloc Sud, and Paramaque deposits is in gold-bearing quartz veins where pyrite is rare or absent. These tourmalines occur in tholeiitic host rocks and are characterized by a high Fe content in the Y-site because Fe is not partitioned in co-precipitating Fe-sulfides; Mg/(Mg+Fe) ratios are below 0.5, which together with low X-site vacancies yield a schorl composition for Sigma 2, Bloc Sud, and Paramaque tourmalines (Fig. 4C). In contrast, Type II tourmaline from the Siscoe and Brosnor deposits, which contains pyrite, is characterized by a Fe content in the Y-site similar to most Type I tourmaline and a Mg/(Mg+Fe) ratio above 0.5, indicating a dravitic composition (Fig. 4C). Type III tourmaline occurs in quartz veins containing arsenopyrite and/or pyrrhotite. Because Fe is partitioned into these sulfides, Type III tourmaline has a low Fe content in the Y-site and a Mg/(Mg+Fe) ratio above 0.5, and with small vacancies in the X-site, yields a dravitic composition (Fig. 4C).

Type I tourmaline from deposits in calc-alkaline host rocks generally lacks major chemical variations among trace elements, with the exception of tourmaline from the D zone of the Goldex deposit and the Parallel Zone of the Lamaque Sud gold project that are characterized by a higher Cr content. In contrast, the chemical signature of Type II tourmaline from deposits in mafic tholeiitic rocks is characterized by an enrichment in V, Cr, Mn, Fe, Co, Ni, Zn, and Sn, compared to Type I tourmaline. These elements are typically high in mafic-ultramafic rocks, suggesting that the trace elements in tourmaline reflect the chemistry of the mafic-ultramafic host rocks. Type III tourmaline from the Lapa deposit shows similar major element contents as in Type I tourmaline, but its trace elements concentrations are slightly higher for Li, Mn, and Pb.
7.2 Discriminating tourmaline compositions using PCA

Principal component analysis of LA-ICP-MS data discriminates Type I tourmaline from deposits hosted in calc-alkaline rocks from Type II tourmaline in tholeiitic rock-hosted deposits (Fig. 9). Sigma 2 tourmaline is distinguished from Type II tourmaline by Mn, V, Ni, Zn, and Ga contents. Type III tourmaline from the Lapa and Orenada deposits cannot be discriminated from Type I tourmaline using this PCA. Results show a distinct chemical signature for Type I and II tourmalines, indicating that Li, K, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Sr, Sn, and Pb are discriminanting elements for orogenic gold tourmalines. The results also reveal an enrichment in V, Cr, Mn, Fe, Co, Ni, Zn, and Sn in most Type II tourmaline from deposits hosted in mafic tholeiitic rocks.

PCA of tourmaline chemistry from the Val-d’Or district with those of various deposit types (Figs. 10, 11) suggests that Val-d’Or tourmaline has a unique chemical signature despite the fact that Type I, II, and III tourmalines differ compositionally at the district scale. Furthermore, tourmaline from the Val-d’Or district and from various orogenic gold deposits elsewhere shares a similar chemical signature, which differs from that of tourmaline from other deposit types. Tourmaline from orogenic gold deposits is characterized by a low metal content compared to tourmaline from massive sulfide deposits. Tourmaline from the Yunlong (Sn), Asarcık (Pb-Zn-Cu±U), and various massive sulfide deposits (Cu±Zn and Pb-Zn±Cu) is characterized by higher Sn, Zn, Cu, and Pb contents than orogenic gold tourmaline, reflecting the metal assemblage of the deposit. Tourmaline from the Tsa da Glisza emerald deposit has higher contents of Li, Be, Ca, Cr, Mn, and Sn compared to tourmaline from orogenic gold deposits of the Val-d’Or district. Galbraith et al. (2009) demonstrated that tourmaline from samples closely associated with emerald has high Cr and V contents. In contrast, the Be content in tourmaline associated with emerald mineralization is higher in Tsa da Glisza samples, likely because tourmaline and beryl were co-precipitating from a Be-rich fluid. Tourmaline associated with emerald mineralization forms a cluster in PC1-PC2 (Fig. 11A), differing from orogenic gold tourmaline by higher contents of Mn, Ca, Sn, and Cr. The Be and Li contents in Tsa da Gliza tourmaline are higher than in Val-d’Or tourmaline, but these elements are excluded in the PCA because these chemical element concentrations are not available for all deposits.

Tourmaline from the pegmatitic and hydrothermal systems of the Schwarzwald area (Germany) is characterized by higher contents of Al, Mn, Fe, K, Zn, and Sn and by lower Mg, Cu, and Sr than tourmaline from orogenic gold deposits of the Val-d’Or district. Furthermore, Schwarzwald pegmatitic tourmaline has higher Mn, Fe, and Zn contents but lower Mg, Ca, Sr contents compared to hydrothermal tourmaline of the Schwarzwald area. Pegmatite tourmaline generally has a lower Mg/(Mg+Fe) ratio than hydrothermal tourmaline. Marks et al. (2013) suggested that the content of trace elements in pegmatitic and hydrothermal tourmalines is controlled by tourmaline-melt and tourmaline-fluid partitioning. Data for tourmaline from the pegmatitic and hydrothermal systems of the Schwarzwald area form two distinct clusters in PC1-PC2 (Fig. 11A) and both can be discriminated from those of the orogenic gold tourmalines.
7.3 Tourmaline in till: applications to mineral exploration

In the Val-d’Or district, tourmaline occurs only within the gold-bearing quartz veins. Tourmaline has been reported in pegmatite of the Preissac-La Corne batholith and in wacke and pelite of the Cadillac Formation, located, respectively, northwest and southwest of the study area (Boily 1995; Desrochers et al. 1996). The PCA results show that a high proportion of till tourmaline carries the chemical signature of tourmaline from the orogenic gold deposits of the district, with a majority showing the signature of Type I tourmaline hosted in calc-alkaline intrusive rocks. Data for only a few tourmaline grains plot in the field of Type II tourmaline hosted in tholeiitic mafic rocks. Orogenic gold deposits hosted in calc-alkaline rocks predominate in the area of the till sample transect. With the exception of the Paramaque deposit, all other tholeiitic-hosted orogenic gold deposits (Sigma 2, Brosnor, Siscoe, Bloc Sud) are located more than 8 km east or west of the till sample transect, suggesting that Type II tourmaline from those deposits was not incorporated into the till along the transect. In Figure 9B, 75% of the data for till tourmaline from sample 14-DG-004 plot in the field defined by Type II tourmaline. Till sample 14-DG-004 is 0.75 km down-ice of the Paramaque deposit, which contains Type II tourmaline. Tourmaline grains recovered in till sample 14-DG-001, located north of the district, carry the chemical signature of the orogenic gold deposits, thus suggesting the presence of undiscovered gold mineralization up-ice. Several gold showings containing tourmaline, located 5 to 20 km north of the Val-d’Or district, are reported in the Québec Government geominning information system.

Composition of till tourmaline from the Val-d’Or district has been projected on the PCA model from various rock and deposit types (Figs. 10B, 11B). The PCA results show that the large majority of tourmaline grains recovered from till samples carries the chemical signature of orogenic gold deposits, with no tourmaline compositions falling in the field defined by tourmaline from other rock or deposit types, which suggests that till tourmaline is unlikely to be derived from other deposit types. These results demonstrate the potential of tourmaline chemistry to be an exploration tool for orogenic gold deposits and also the ability of PCA to determine the provenance of the grains by classifying different tourmaline compositions, as shown in the Meliadine area of Nunavut, Canada (Manéglia et al. 2018).

7.4 Discriminating scheelite compositions using PCA

PCA of LA-ICP-MS data discriminates scheelite from orogenic gold deposits of the Val-d’Or district by delineating three clusters, one for each sample location (Sigma, Beaufor, and Triangle Zone; Fig. 12). Scheelite from the Sigma deposit is distinguished from Beaufor scheelite by higher Mg, S, K, Mn, and Pb contents and lower
V, Cu, Sr, Nb, and Mo contents. Scheelite from the Triangle Zone shows higher K, V, Zn, As, Sr, and Pb and lower Mn and Nb compared to scheelite from the Sigma and Beaufor deposits. PCA results (Figs. 13, 14) are useful for discriminating the chemistry of scheelite in the Val-d’Or district and from other orogenic gold deposits (Hazarika et al. 2016; Scuba et al. submitted) from W-Mo skarn deposits (Song et al. 2014). Val-d’Or scheelite has a chemical signature similar to that from deposits hosted in the Abitibi greenstone belt, characterized by high Na, Y, and REE contents, with the exception of scheelite from the Canadian Malartic deposit that has lower Na, Y, and REE, but higher Sr, Pb, U, Th, and Mo contents (Fig. 16). Sigma, Beaufor, Triangle Zone, Dome, and Young Davidson are hosted in mafic to felsic metagneous rocks, whereas the Canadian Malartic deposit is within clastic metasedimentary rocks. Higher concentrations of Na, REE, and Y in scheelite from deposits hosted in felsic to mafic rocks are caused by the greater abundance of Na-feldspar in these host rocks. Scheelite from the Val-d’Or district has high concentrations of MREE and HREE (Fig. 14) and thus can be distinguished from scheelite occurring in W-Mo skarn deposits and from other gold deposits, including Crusader, Kockar, Kumtor, and Canadian Malartic, whereas Nevoria has also been classified as a skarn deposit.

7.5 Scheelite in till: applications to mineral exploration

PCA models defined by LA-ICP-MS scheelite data are used here to classify the provenance of scheelite grains recovered in till samples (Fig. 12B). In the Val-d’Or district, scheelite occurs only within the gold-quartz veins and has not been reported in other lithologies. The PCA results show that till scheelite carries the chemical signature of scheelite from the Beaufor and Triangle Zone deposits. No till scheelite compositions plot in the field defined by Sigma scheelite. The Beaufor deposit is located less than 1 km north of sample 14-DG-002 and 18 km northeast of sample 14-DG-003. Both till samples containing scheelite grains are located down-ice of the Beaufor deposit. The Sigma and Triangle Zone deposits are located 14 km west of the till sampling transect, suggesting that scheelite recovered in the till samples is unlikely to carry the chemical signature of scheelite from those two deposits. However, one of the scheelite grains from sample 14-DG-002 shows a chemical signature similar to that of scheelite from the Triangle Zone (Fig. 12B), raising the possibility that an undiscovered Triangle Zone-like deposit occurs up-ice of sample 14-DG-002. This interpretation must be taken with caution, however, because it is based on data for only a single scheelite grain.

Till scheelite from the Val-d’Or district is projected on PCA defined by scheelite data from other deposit types including orogenic gold, other gold mineralization, and W-Mo skarn (Figs. 13B, 14B). The PCA results show that till scheelite carries the chemical signature of orogenic gold deposits, with no scheelite having the signature of scheelite from other deposit types. In Figure 13, two scheelite grains from till samples 14-DG-002 and 14-DG-003 display a chemical signature similar to that of scheelite from the up-ice Beaufor deposit.
7.6 Magnetite in till: applications to mineral exploration

Hydrothermal magnetite from orogenic gold deposits of the Val-d’Or district is characterized by higher concentrations of Cr, Zn, Mn, K, Ca, Ti, and Al relative to magmatic magnetite from the intrusive host rocks. No hydrothermal magnetite has the signature of Ni-Cu-PGE deposits, with the exception of that from the Louvicourt deposit (Fig. 8A). Hydrothermal magnetite shows a higher Ca+Al+Mn content than magmatic magnetite, excluding two magnetite grains from the Louvicourt deposit (Fig. 8C). Magnetite is rare in orogenic gold deposits of the Val-d’Or district and occurs as finely disseminated grains (<0.05 mm), which indicates that most magnetite recovered in the 0.5 to 2.0 mm grain-size ferromagnetic fraction of the till samples probably did not originate from the gold-bearing quartz veins. Magnetite recovered in glacial till shows the chemical signature of both hydrothermal and magmatic magnetite with almost no till magnetite having the signature of Ni-Cu-PGE deposits, with the exception of sample 14-DG-002 (Fig. 8B) where few magnetite grains show the chemical signature of Ni-Cu-PGE deposits. However, the provenance of magnetite recovered from glacial till is not clearly identified in this study, and hence the use of magnetite as an exploration tool for orogenic gold deposits is inconclusive for the Val-d’Or district.

8. Conclusions

Tourmaline from orogenic gold deposits of the Val-d’Or district has a dravite-schorl composition and is characterized by concentric zoning whereby the core (blue) has higher Si, Al, and Mg contents and lower Fe, Ca, Ti, K, V, Sr, Pb, and REE contents than the rim (brown). Chondrite-normalized REE data display two patterns: (1) flat showing an enrichment in HREE with a positive Eu anomaly, which is typically characteristic of the core; and (2) flat showing a slight enrichment of LREE with a positive Eu anomaly, which is generally characteristic of the rim. The Fe content in the tourmaline is likely controlled by the co-precipitation of Fe-sulfides, whereas the content of trace elements chiefly reflects the composition of the host rock. Principal component analysis indicates that Type I and III tourmalines are distinguished from Type II tourmaline, and that tourmaline from orogenic gold deposits can be discriminated from tourmaline occurring in other deposit types. Most till-hosted tourmaline grains from the Val-d’Or district have the signature of orogenic gold deposit tourmaline and of Type I tourmaline from deposits in calc-alkaline host rocks. The results reveal the potential of tourmaline chemistry as an exploration tool for orogenic gold deposits.

Scheelite from orogenic gold deposits of the Val-d’Or district is generally homogeneous in cathodoluminescence response and lacks zonation. Chondrite-normalized REE data have a bell-shaped pattern with a positive or negative Eu anomaly reflecting the composition of the hydrothermal fluid or host rock. Scheelite from
the Val-d’Or district carries the signature of orogenic gold deposits hosted in felsic to intermediate-composition rocks. Till scheelite from the Val-d’Or district is characterized by the signature of orogenic gold deposits hosted in felsic to intermediate-composition rocks, and specifically by the signature of scheelite from the Beaufor and Triangle Zone deposits. The chemistry of scheelite has the potential to be an useful exploration tool for orogenic gold deposits.

Magnetite is rare in orogenic gold deposits of the Val-d’Or district and occurs as finely disseminated grains, smaller than that of the ferromagnetic fraction studied here (0.5-2.0 mm). The relatively large size (>0.5 mm) of magnetite grains in the glacial till suggests that this magnetite probably does not originate from the gold-bearing quartz veins, consistent with the chemical signature of magnetite till.

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Appendix A: Relevant geological information for deposits reported in this study

<table>
<thead>
<tr>
<th>Number</th>
<th>Deposit</th>
<th>Location</th>
<th>Age of mineralization</th>
<th>Mineralization</th>
<th>Host rocks</th>
<th>Metamorphic grade</th>
<th>Indicator minerals</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lapa</td>
<td>Rivière-Heva, Québec</td>
<td>≤ 2684 Ma</td>
<td>1) Finely disseminated auriferous Au-As-Pb-Zn veins in altered wall rocks and 2) native gold ± Sb-bearing minerals in folded Gt-Dol-Cal veinlets and in altered wall rocks</td>
<td>Grauwackes, pelitic schists and polymictic conglomerates (Cadillac Group) and tholeiitic basalts, porphyric andesites, calc-alkaline tufts, and komatiites crosscut by felsic to mafic dikes and sills (Piche Group)</td>
<td>Upper greenschist to lower amphibolite</td>
<td>Tur</td>
<td>Simard (2011) &amp; Simard et al. (2013)</td>
</tr>
<tr>
<td>2</td>
<td>Kena</td>
<td>Val-d’Or, Québec</td>
<td>≥ 2686 Ma</td>
<td>Multistage Cb-Qz-Ab-Py stringer, stockwork, breccia, and replacement vein system confined within the albite swarm and (e. g. Maine ore zone, K zone) occurring in folded extensional veins and late Qz-Cb veins (e. g. C Vein) occurring in a shear zone</td>
<td>Albite dike swarm (dioritic) and tholeiitic basalts/komatiites (Jacoba Formation)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>Perrault (1987) &amp; Morasse et al. (1995)</td>
</tr>
<tr>
<td>3</td>
<td>Siscoe</td>
<td>Val-d’Or, Québec</td>
<td>≥ 2686 Ma &amp; ≤ 2684 Ma</td>
<td>Qz-Tur-Cb veins occurring in a shear zone and (e. g. Maine ore zone, K zone) occurring in folded extensional veins and late Qz-Cb veins (e. g. C Vein) occurring in a shear zone</td>
<td>Gabbroic sill (Siscoe stock) hosted in tholeiitic basalts/komatiites (Dubuison Formation)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>Truxel (1985b), Olivo and Williams-Jones (2002) &amp; Olivo et al. (2007)</td>
</tr>
<tr>
<td>4</td>
<td>Goldex</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb veins occurring in a shear zone and (e. g. Maine ore zone, K zone) occurring in folded extensional veins and late Qz-Cb veins (e. g. C Vein) occurring in a shear zone</td>
<td>Qz-Tur-Cb veins occurring in a shear zone</td>
<td>Greenschist</td>
<td>Tur, Mag</td>
<td>SIGÉOM**</td>
</tr>
<tr>
<td>5</td>
<td>Vein No. 5</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb veins occurring in a shear zone and (e. g. Maine ore zone, K zone) occurring in folded extensional veins and late Qz-Cb veins (e. g. C Vein) occurring in a shear zone</td>
<td>Qz-Tur-Cb veins occurring in a shear zone</td>
<td>Greenschist</td>
<td>Hem</td>
<td>Barbe (2011)</td>
</tr>
<tr>
<td>6</td>
<td>Sigma</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb veins occurring in a shear zone and (e. g. Maine ore zone, K zone) occurring in folded extensional veins and late Qz-Cb veins (e. g. C Vein) occurring in a shear zone</td>
<td>Qz-Tur-Cb veins occurring in a shear zone</td>
<td>Greenschist</td>
<td>Tur, Sch</td>
<td>SIGÉOM**</td>
</tr>
<tr>
<td>7</td>
<td>Lamaque Sud</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb veins occurring in a shear zone and (e. g. Maine ore zone, K zone) occurring in folded extensional veins and late Qz-Cb veins (e. g. C Vein) occurring in a shear zone</td>
<td>Qz-Tur-Cb veins occurring in a shear zone</td>
<td>Greenschist</td>
<td>Tur</td>
<td>SIGÉOM**</td>
</tr>
<tr>
<td>8</td>
<td>Audet</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb veins occurring in a shear zone and (e. g. Maine ore zone, K zone) occurring in folded extensional veins and late Qz-Cb veins (e. g. C Vein) occurring in a shear zone</td>
<td>Qz-Tur-Cb veins occurring in a shear zone</td>
<td>Greenschist</td>
<td>Tur</td>
<td>SIGÉOM**</td>
</tr>
<tr>
<td>9</td>
<td>Nord-Ouest*</td>
<td>Val-d’Or, Québec</td>
<td>-</td>
<td>-</td>
<td>Grauwackes, silstone, minor mudstone, sandstones, and conglomerate lens sandwiched between the low strain-volcanic rocks of the Heva formation and the Cadillac Group (Val-d’Or Formation)</td>
<td>Upper greenschist to lower amphibolite</td>
<td>Tur</td>
<td>Pitre (2000) &amp; Desrochers and Robert (2000), Rezeau et al. (2007)</td>
</tr>
<tr>
<td>10</td>
<td>Orenada</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Apy veins</td>
<td>Quartz diorite (Orenada batholith)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>Neumayr et al. (2000) &amp; Neumayr et al. (2007)</td>
</tr>
<tr>
<td>11</td>
<td>Lac Herbin</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb subvertical veins having extensional veins occurring in a shear zone</td>
<td>Quartz diorite (Boulamaque Batholith)</td>
<td>Greenschist</td>
<td>Tur, Hem</td>
<td>Rezeau (2012) &amp; Rezeau et al. (2017)</td>
</tr>
<tr>
<td>12</td>
<td>Paranaque</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb veins occurring in a shear zone</td>
<td>Quartz diorite and gabro (Lamaque batholith) hosted in mafic to felsic volcanic rocks (Heva formation)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>Neumayr et al. (2000) &amp; Neumayr et al. (2007)</td>
</tr>
<tr>
<td>13</td>
<td>Carney (north)*</td>
<td>Val-d’Or, Québec</td>
<td>-</td>
<td>-</td>
<td>Quartz diorite (Boulamaque Batholith)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>Pitre (2000)</td>
</tr>
<tr>
<td>14</td>
<td>Snowbank</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb veins occurring in a shear zone</td>
<td>Quartz diorite (Boulamaque Batholith)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>SIGÉOM**</td>
</tr>
<tr>
<td>15</td>
<td>O’connell</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb veins occurring in a shear zone</td>
<td>Quartz diorite and gabro (Lamaque batholith) hosted in mafic to felsic volcanic rocks (Heva formation)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>SIGÉOM**</td>
</tr>
<tr>
<td>16</td>
<td>Beauroir</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb subvertical veins having extensional veins occurring in a shear zone</td>
<td>Quartz diorite (Boulamaque Batholith)</td>
<td>Greenschist</td>
<td>Tur, Mag</td>
<td>SIGÉOM**</td>
</tr>
<tr>
<td>17</td>
<td>Lucien Béliveau/New Beliveau</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb subvertical veins having extensional veins occurring in a shear zone</td>
<td>Microcline dikes and mafic flows intercalated with intermediate volcanic rocks (Dubuison Formation)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>Guimond (1986) &amp; Lafrance (1986)</td>
</tr>
<tr>
<td>18</td>
<td>Brosnor</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb subvertical veins</td>
<td>Gabbroic sill and tholeiitic basalts/komatiites (Jacoba Formation)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>Gaudreau et al. (1988)</td>
</tr>
<tr>
<td>19</td>
<td>Buffaloid</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb veins occurring in a shear zone</td>
<td>Gabbroic sill and tholeiitic basalts/komatiites (Jacoba Formation)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>SIGÉOM**</td>
</tr>
<tr>
<td>20</td>
<td>Sigma 2</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb subvertical veins having extensional veins occurring in a shear zone</td>
<td>Gabbroic sill (Sigma 2)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>Hebert et al. (1988) &amp; Hebert et al. (1991)</td>
</tr>
<tr>
<td>21</td>
<td>Bloc Sud</td>
<td>Val-d’Or, Québec</td>
<td>≤ 2684 Ma</td>
<td>Qz-Tur-Cb veins occurring in a shear zone</td>
<td>Gabbroic sill (Sigma 2)</td>
<td>Greenschist</td>
<td>Tur, Mag</td>
<td>SIGÉOM**</td>
</tr>
<tr>
<td>22</td>
<td>Lac Simon*</td>
<td>Val-d’Or, Québec</td>
<td>-</td>
<td>-</td>
<td>Gabbroic sill (Sigma 2)</td>
<td>Greenschist</td>
<td>Tur</td>
<td>Pitre (2000)</td>
</tr>
</tbody>
</table>

* Deposit information not available in the literature. Sample from Pitre (2000).
** Spatial reference geostatistical information system (SIGÉOM) containing the entire Québec geoscientific database.
Figure captions (colors online only)

Figure 1 (double) - Simplified regional geological map of Val-d’Or orogenic gold district showing distribution of quartz-tourmaline-carbonate-gold veins and till samples used in this study and local ice-flow directions (yellow arrows). Numbers in figure refer to gold deposits as follows: 1: Lapa; 2: Kiena; 3: Siscoe; 4: Goldex; 5: Vein No. 5; 6: Sigma; 7: Lamaque Sud; 8: Audet; 9: Nord-Ouest; 10: Orenada; 11: Lac Herbin; 12: Paramaque; 13: Snowbank; 14: Canmet (nord); 15: O’Connell; 16: Beaufor; 17: Lucien Béliveau/New Béliveau; 18: Brosnor; 19: Buffadison; 20: Sigma 2; 21: Bloc Sud; 22: Lac Simon. See Appendix I for summary of relevant geological information for each deposit. Geological map modified from Beaudoin and Pitre (2005); ice-flow directions after Paradis (2007).

Figure 2 (1.5) - Proportion of indicator minerals recovered from till samples relative to distance for (A) gold grains recovered in till normalized to 10 kg samples; (B) tourmaline and scheelite grains recovered in 0.25 to 0.5 mm HMC fraction normalized to 10 kg samples; and (C) magnetite, hematite, titanomagnetite, ilmenite, and chromite grains recovered from 0.5 to 2.0 mm ferromagnetic fraction. Symbolised samples are 14-DG-001 (-15 km); 14-DG-002 (-12 km); 14-DG-005 (-6 km); 14-DG-004 (-2 km); Larder Lake-Cadillac Fault Zone (0 km); 14-DG-003 (4 km). Gray zone represents limits of Val-d’Or district. Mineral abbreviations: Chr, chromite; Hem, hematite; Ilm, ilmenite; Mag, magnetite; Sch, scheelite; Ti-Mag, titanomagnetite; Tur, tourmaline.

Figure 3 (double) - Photographs and microphotographs of tourmaline, scheelite, and magnetite textures from gold-quartz veins and till samples of Val-d’Or district (B, C, D, E, H and I are under plane-polarized light; J, K and L are under reflected light). (A) Black euhedral needles of tourmaline in quartz-tourmaline vein (Goldex). (B) Concentrically and sector-zoned tourmaline (Lac Herbin). (C) Oscillatory zoned tourmaline (New Béliveau). (D) Patchy zoned tourmaline (Goldex). (E) Poikilitic tourmaline with quartz inclusions (Goldex). (F) Till tourmaline from glacial sediment sample 14-DG-002. (G) Beige subhedral to euhedral crystal of scheelite in quartz-tourmaline vein (Beaufor). (H) Aggregate of scheelite crystals associated with tourmaline (Beaufor). (I) Scheelite associated with tourmaline (Sigma). (J) Magnetite inclusions in pyrite from an EPD sample (Goldex). (K) Euhedral magnetite with chromite core in diorite (Beaufor). (L) Finely disseminated magnetite grains in foliated intermediary volcanics clast recovered in till. Mineral abbreviations: Chr, chromite; Mag, magnetite; Py, pyrite; Qz, quartz; Sch, scheelite; Tur, tourmaline.
Figure 4 (double) - Classification of tourmaline from gold-quartz veins (A, C) and till (B, D) of Val-d’Or district. (A) X-site vacancy-Ca-(Na+K) ternary diagram for tourmaline occurring in gold-quartz veins. (B) Till tourmaline data plotted on same ternary diagram as in (A). (C) Vacancy/(Vacancy+Na+K) vs Mg/(Mg+Fe) diagram for tourmaline in gold-quartz veins. (D) Till tourmaline data plotted on same diagram as in (C). Compositional diagrams after Henry et al. (2011).

Figure 5 (1.5) - Element variation diagrams for tourmaline from gold-quartz veins of Val-d’Or district. (A) Mg/(Mg+Fe) vs Sc. (B) Mg/(Mg+Fe) vs V.

Figure 6 (double) – Chondrite-normalized REE patterns in tourmaline from gold-quartz veins of Val-d’Or district. (A) Flat patterns showing an enrichment in HREE with positive Eu anomaly. (B) Flat patterns showing slight enrichment of LREE with positive Eu anomaly. (C) Microphotograph of concentrically zoned tourmaline grain (Beaufor). Double line is the LA-ICP-MS analysis trench (D) Core and rim of tourmaline grain in (C) shows REE patterns of A and B, respectively. (E) Till tourmaline characterized by REE pattern A. (F) Till tourmaline characterized by REE pattern B. Chondrite data from Taylor and McLennan (1985).

Figure 7 (double) – Chondrite-normalized REE patterns for scheelite from gold-quartz veins of Val-d’Or district. (A) Bell-shaped REE patterns with positive Eu anomaly (Sigma). (B) Bell-shaped patterns with small negative Eu anomaly (Beaufor). (C) Bell-shaped patterns with small negative Eu anomaly (Triangle Zone). (D) Till scheelite characterized by bell-shaped patterns with small negative Eu anomaly. Chondrite data from Taylor and McLennan (1985).

Figure 8 (double) - Magnetite compositional diagrams. (A) Ni+Cr vs Si+Mg plot for magnetite occurring in gold-quartz veins and intrusive host rocks. (B) Till magnetite data plotted on same diagram as in (A). (C) Ca+Al+Mn vs Ti+V plot for magnetite occurring in gold-quartz veins and intrusive host rocks. (D) Till magnetite data plotted on same diagram as in (C). Compositional diagrams after Dupuis and Beaudoin (2011).

Figure 9 (single) – (A) Principal component analysis results (PC1-PC3) of LA-ICP-MS data for tourmaline from orogenic gold deposits of Val-d’Or district. (B) Till tourmaline data projected on PC1-PC2.
Figure 10 (double) – (A) Principal component analysis results (PC1-PC2) for tourmaline from various deposit types including orogenic gold (this study; Hazarika et al. 2015; Hazarika et al. 2016; Jiang et al. 2002; Deksissa and Koeberl 2002), vein-type Sn (Jiang et al. 2004), Cu-Mo porphyry (Iveson et al. 2016), and vein-type Pb-Zn-Cu ± U (Yavuz et al. 2011). (B) Till tourmaline data projected on PC1-PC2.

Figure 11 (double) - (A) Principal component analysis results (PC1-PC2) for tourmaline from various deposit types including orogenic gold of Val-d’Or district (this study), massive sulfide (Griffin et al. 1996; Slack et al. 1999), tourmalinite (Griffin et al. 1996), and emerald (Galbraith et al. 2009), and from pegmatitic and hydrothermal systems of Schwarzwald area (Marks et al. 2013). (B) Till tourmaline data projected on PC1-PC2.

Figure 12 (single) - (A) Principal component analysis results (PC1-PC2) of LA-ICP-MS data for scheelite from orogenic gold deposits of Val-d’Or district. (B) Till tourmaline data projected on PC1-PC2.

Figure 13 (double) - (A) Principal component analysis results (PC1-PC2) for scheelite from various orogenic gold deposits (this study; Sciuba et al. submitted). (B) Till tourmaline data projected on PC1-PC2.

Figure 14 (double) – (A) Principal component analysis results (PC1-PC2) for scheelite from various orogenic gold deposits (this study; Hazarika et al. 2016; Sciuba et al. submitted) and skarn deposits (Song et al. 2014). (B) Till tourmaline data projected on PC1-PC2.