



Fluid-rock sulfidation reactions control Au-Ag-Te-Bi precipitation in the Val-d'Or orogenic gold vein field (Abitibi subprovince, Canada)

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Abstract

The Val-d'Or vein field (VVF), located in the southern Abitibi subprovince (Québec, Canada), is host to ~47 Moz gold and is therefore an example of a greenstone-hosted orogenic gold district. Gold is contained in quartz-tourmaline-carbonate veins that cut As-poor intermediate to mafic volcanic and intrusive rocks, including dioritic, granodioritic and gabbroic sills, dikes, stocks, and plutons. Five investigated orebodies (Goldex, Triangle, Plug #4, Pascalis Gold Trend, Beaufor) host gold in vein- and wallrock-hosted pyrite-rich sulfide aggregates (> 95 vol%) that show a porous core domain (Py1), with abundant inclusions of carbonate, silicate, and Fe-oxides up to several tens of μm in size. A homogeneous pyrite rim domain (Py2) surrounds Py1 and contains most of the gold as native gold and polymetallic (Au-Ag-Te-Bi) inclusions, primarily calaverite and petzite. The two pyrites show different Au and As contents (Py1 = Au $\leq$ 30 ppm; As $\leq$ 67 ppm; Py2 = Au $\leq$ 1250 ppm; As $\leq$ 550 ppm). Pyrite shows a ubiquitous shift in $\delta^{34}\text{S}$ values of up to +3.0‰ from Py1 ($\delta^{34}\text{S} = -0.4\text{‰}$ to 5.8‰, $n = 32$) to Py2 ($\delta^{34}\text{S} = 0.0\text{‰}$ to 6.3‰, $n = 59$) and records a small, slightly negative $\Delta^{33}\text{S}$ signature between -0.20‰ and 0.01‰ . The $\delta^{34}\text{S}$ shift suggests that removal of reduced sulfur species from auriferous hydrothermal fluids causes the formation of inclusion-hosted gold in Py2 by a decrease in the fluid sulfur fugacity ($f\text{S}_2$) through wallrock sulfidation of Fe-oxides. The shift also correlates with locally enriched Co and Ni concentrations in Py1 (< 1 wt%), compared to lower, oscillatory zoned concentrations (< 0.1 wt%) in Py2, respectively, indicating an overall decrease in fluid oxygen fugacity ($f\text{O}_2$). Contemporaneously, a decrease in fluid tellurium fugacity ($f\text{Te}_2$) drives polymetallic inclusion-hosted gold formation in Py2, initially as calaverite followed by increasingly Ag-bearing petzite and hessite. The multiple sulfur isotopes and trace element compositions recorded in pyrite in the VVF indicate that a homogeneous fluid reservoir introduced gold-sulfide complexes. Even if considered a localized process at the ore-shoot scale, fluid-wallrock sulfidation reactions can lead to a coupled decrease in $f\text{S}_2$, $f\text{O}_2$, and $f\text{Te}_2$ of auriferous hydrothermal fluids in a greenstone-hosted As-poor gold district.

Keywords Archean · Orogenic gold · Multiple sulfur isotopes · Sulfide trace elements · Abitibi subprovince

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Introduction

Orogenic gold mineralization accounts for more than 6573 Moz of Au, or 41% of historic global gold production, and is widely accepted to occur along high-angle reverse shear zones that channel fluids by repeated fault-valve processes during cyclic supralithostatic fluid pressure fluctuations (Sibson et al. 1988; Sibson and Scott 1998; Lipson 2014; Cox 2016). These brittle-ductile shear zones develop primarily in the middle to upper crust during compressional periods, and quartz-carbonate veins commonly form along the retrograde path of an orogenic cycle, and post-date peak metamorphic conditions by up to 80 million years (Groves 1993, 2003; Groves et al. 2005; Condie 2000; Kerrich et al. 2000; Goldfarb et al. 2001, 2005; Bierlein

et al. 2006; Groves and Santosh 2016; Herzog et al. 2023). Hydrothermal events associated with an orogenic cycle have the potential to release metamorphic and/or magmatic fluids that accumulate at < 10 km depth, below the brittle-ductile transition. At the gold precipitation site, key fluid mechanisms such as pressure variations, fluid mixing, or fluid-wallrock reactions have been considered main drivers to cause orogenic gold formation (Phillips 1986; Colvine 1989; Hodgson and Hamilton 1989; Hodgson 1993; Robert 1997; Robert et al. 2005; Ward et al. 2017; Sugiono et al. 2022). Many orogenic gold deposits are hosted in meta-sedimentary rocks. In such cases, gold is commonly hosted by As-rich pyrite (> 1 wt%) and/or arsenopyrite. An increase in As leads to efficient lattice-bound gold deposition in As-rich pyrite through coupled Au-As redox reactions (Reich et al. 2005; Pitcairn et al. 2006; Pokrovski et al. 2019, 2021; McDivitt et al. 2022; Sugiono et al. 2022). In contrast, many greenstone gold districts are dominated by As-poor mafic volcanic rocks, such as in the Xiaolinling district (North China Craton), Mt Pleasant district (Yilgarn Craton), Timmins-Porcupine (Superior Craton), or Hope Bay belt (Slave Craton), indicating that As is not a requirement for orogenic gold formation (Bi et al. 2011; Sherlock et al. 2012; LaFlamme et al. 2018b; Dubé and Mercier-Langevin 2020; Dubé et al. 2020). This implies that physico-chemical processes, which occur during crustal fluid advection in As-poor mafic volcanic and sedimentary rocks and that lead to highly localized sulfide and gold precipitation in veins, remain to be fully understood at the sulfide grain scale.

Based on a detailed paragenetic sequence, in situ micro-analytical techniques have the potential to elucidate physico-chemical processes that result in the precipitation of gold and gold-bearing sulfides. Changes in fluid chemistry leading to gold precipitation may be constrained based on textural observations in combination with high-resolution multiple S isotope and trace element composition of gold-hosting sulfides (e.g., LaFlamme et al. 2018c; Sugiono et al. 2022). Two physico-chemical parameters have a strong effect on Au solubility: the fluid sulfur (fS_2) and oxygen (fO_2) fugacities. Changes in fS_2 and fO_2 of a hydrothermal fluid influence the $\delta^{34}S$ signature, the minor and trace element composition, including gold-bisulfide complex solubility (Pokrovski et al. 2014, 2015, 2022), precipitated sulfides and associated phases (e.g., Sugiono et al. 2022). Other important parameters to monitor local physico-chemical processes include variations of Co and Ni concentrations, which show both an increased solubility at higher fO_2 conditions and can provide additional information on fO_2 fluctuations at the time of sulfide deposition (Peterson and Mavrogenes 2014; Fougereuse et al. 2016; Ward et al. 2017; Daver et al. 2020; Jansson and Liu 2020; Sugiono et al. 2022).

In this study, we present textural evidence, multiple sulfur isotopes, and trace element compositions of Au-bearing

sulfides from five orebodies (Goldex, Triangle, Plug #4, Pascalis Gold Trend and Beaufor) to understand which common physico-chemical fluid processes at the mineral grain scale can control gold precipitation throughout the world-class Val-d'Or vein field (VVF) in the southern Abitibi subprovince, Québec, Canada.

Regional geological setting

The southeastern margin of the Superior Craton (Fig. 1a) comprises two subprovinces, the Abitibi and the Pontiac, that are structurally juxtaposed along the Larder Lake-Cadillac fault zone (LLCfz; Fig. 1b). The Abitibi subprovince comprises greenstone belts consisting of volcano-sedimentary rocks intruded by granitic plutons and, in general, metamorphosed to the sub-greenschist and locally up to amphibolite facies. The ultramafic, mafic, and felsic submarine volcanic sequences were deposited between ca. 2795 and 2695 Ma, and the volcanic successions were intruded by plutons of tonalitic, granodioritic, dioritic, and monzonitic compositions between ca. 2750 and 2630 Ma (Latulippe 1966; Pyke et al. 1973; Dimroth et al. 1978, 1983; Hyde 1980; Scott et al. 2002; Ross et al. 2011a, b; Dubé and Mercier-Langevin 2020). The Pontiac subprovince structurally underlies the Abitibi subprovince to the north (Fig. 1b) and consists of sedimentary rocks of the Pontiac Group metamorphosed from upper greenschist to amphibolite facies. The Pontiac Group is composed of turbiditic graywacke and mudstones with lesser ultramafic–mafic volcanic and compositionally varied intrusive rocks (Camiré et al. 1993; Thurston et al. 2008; Piette-Lauzière et al. 2019; Rehm et al. 2021). The Abitibi-Wawa Orogeny affected the two subprovinces throughout a prolonged period of ~ 120 million years from ca. 2700 Ma to 2580 Ma and caused thick-skinned and thin-skinned tectonics with several compressive periods between ≤ 2685 and ≥ 2640 Ma (Moser 1994; Mercier-Langevin et al. 2007; Thurston et al. 2008; Dubé and Mercier-Langevin 2020). Both subprovinces were affected by contemporaneous low- to medium-grade regional metamorphism between ca. ≤ 2669 and ≥ 2643 Ma and ≤ 2665 and 2645 Ma (Machado et al. 1991; Davis et al. 1994; Powell et al. 1995; Piette-Lauzière et al. 2019).

Geological setting of the Val-d'Or vein field

The stratigraphic sequence that hosts the VVF (Fig. 1b) comprises the Malartic and Louvicourt groups (Fig. 2). The oldest unit of the Malartic Group is the La Motte-Vassan Formation (2714 ± 2 Ma), which comprises effusive ultramafic, komatiitic rocks. The overlying Dubuisson Formation (2708 ± 2 Ma) is characterized by ultramafic–mafic

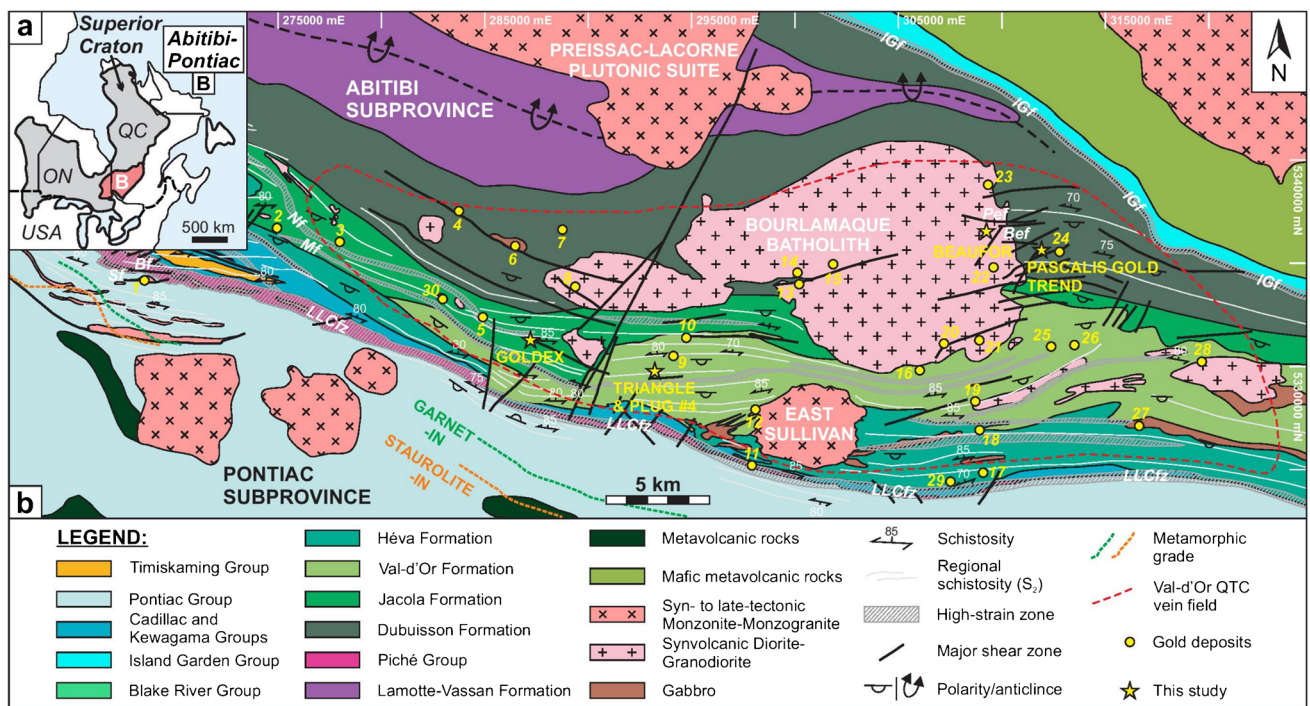


Fig. 1 **a** Map outlining the extent of the Superior Craton and location of the Abitibi and Pontiac subprovinces. **b** Geological map of the area between Malartic and Val-d'Or showing the outline of the Val-d'Or vein field, as well as the studied and other gold deposits (after Wong et al. 1991; Morasse et al. 1995; Pilote et al. 2000; Bedeaux et al. 2017; Montsion et al. 2018; SIGÉOM 2020). Bf=Barnat fault, IGf=Island Garden fault, MF=Marbenite fault, Nf=Norbenite fault, QTC=quartz-tourmaline-carbonate, Sf=Sladen

fault. 1=Canadian Malartic, 2=Camflo, 3=Norlartic, 4=Wesdome, 5=Shawkey, 6=Siscoe, 7=Siscoe Extension, 8=Sullivan, 9=Lamaque, 10=Sigma, 11=Orenada Zone 4, 12=East Sullivan, 13=Bras d'Or, 14=New Formaque, 15=Lac Herbin, 16=Manitou-Barvue, 17=Akasaba, 18=Louvicoourt Goldfield, 19=Dunraine, 20=Wrightbar, 21=Beacon 2, 22=Courvan, 23=Pascal's North, 24=Lucien C. Béliveau, 25=Louvem, 26=Louvicoourt, 27=Sigma 2, 28=Bevcon, 29=Akasaba West, 30=Kiena

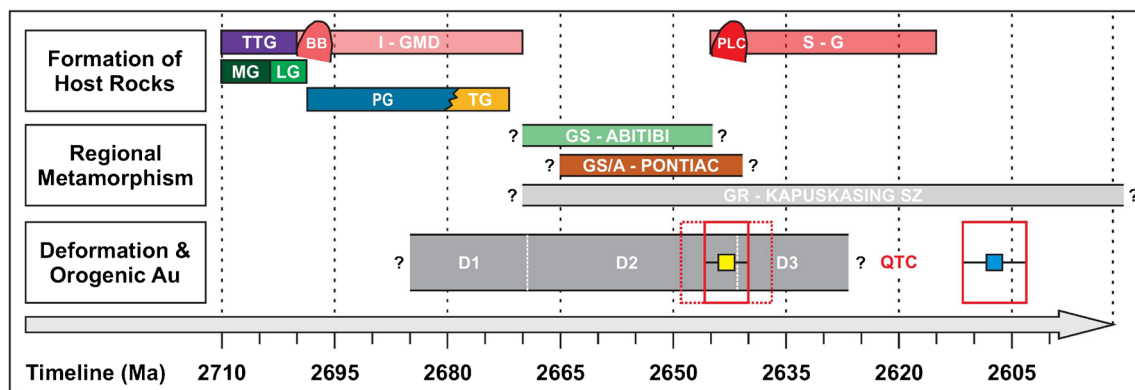


Fig. 2 Simplified timeline reflecting the temporal and structural framework of the Malartic-Val-d'Or district, highlighting the major period of orogenic gold mineralization commonly inferred based on cross-cutting relationships of dikes with faults, shears, fabrics, and structural data in the VVF (c.f. Ayer et al. 2005; Dubé and Gosselin 2007; Bedeaux et al. 2017). In situ analyses of QTC veins (Herzog et al. 2023) define one period of gold deposition and a later period of hydrothermal fluid flow that remobilized gold. A=amphibolite

facies metamorphism, BB=Bourlamaque batholith, GR=granulite facies metamorphism, GS=greenschist facies metamorphism, I-GMD=I-type granodiorite-monzonite-diorite, KSZ=Kapusking Structural Zone, LG=Louvicoourt Group, MG=Malartic Group, PG=Pontiac Group, PLC=Preissac-LaCorne Plutonic Suite, QTC=quartz-tourmaline-carbonate, S-G=S-type granite, TTG=tonalite-trondhjemite-granodiorite

rocks with local felsic rocks (Pilote et al. 2000, 2015). The youngest unit of the Malartic Group, the Jacola Formation (2706 ± 2 Ma), contains mafic volcanic rocks, such as pillow basalts (Machado and Gariépy 1994). The oldest unit of the Louvicourt Group is the Val-d'Or Formation (2704 ± 1 Ma), composed of basaltic pillow lavas and pyroclastic andesitic rocks. The youngest rocks of the Louvicourt Group are the volcanoclastic mafic to felsic rocks of the Héva Formation (2702 ± 2 Ma; Machado and Gariépy 1994; Pilote et al. 2000, 2015).

Tectono-magmatic history of the Val-d'Or vein field

The VVF (Fig. 2) is the result of two major magmatic, two compressive and one transpressive periods during the Abitibi-Wawa Orogeny, which caused regional large-scale folds and fabrics observed (Moser 1994).

A first period of I-type plutonism (Fig. 2) included the 2699.8 ± 1.0 Ma syn-volcanic Bourlamaque batholith, a quartz-granodiorite-diorite (Wong et al. 1991). Near contemporaneous small-scale intrusions include the gabbroic 2693.2 ± 4.7 Ma Plug #4 (Dubé 2018), the 2687 ± 1.2 Ma sill-like Goldex quartz-diorite to granodiorite (David 2019; Munger 2019), the 2685 ± 0.9 Ma Triangle diorite (Dubé 2018), and the 2684 ± 1 Ma East Sullivan monzonite stock (Pilote et al. 1999). Between 2645 and 2613 Ma, a second S-type intrusive period generated the Preissac-LaCorne plutonic suite, located northeast of Val-d'Or (Feng et al. 1992; Kerrich and King 1993; Chown et al. 2002; Davis 2021).

The earliest compressive period D1 (ca. 2685–2669 Ma) is inferred in the Malartic-Val-d'Or district by large-scale folding (F1) and formed structural corridors that are sub-parallel to the LLCfz (Imreh 1984; Corfu 1993; Morasse et al. 1995; Morasse 1998; Dubé and Mercier-Langevin 2020). These F1 folds are only locally observed further in the west in the areas of Rouyn-Noranda (Poulsen 2017) and Timmins (Ferguson et al. 1968; Bleeker 2015), lack axial planar foliation, and are truncated by the Timiskaming unconformity. The second compressive period D2 is the result of N-S shortening that superimposed the regional penetrative foliation (S2) on volcanic bedding (Robert 1989, 1990; Corfu et al. 1991; Bedeaux et al. 2017; De Souza et al. 2017; Dubé and Mercier-Langevin 2020). East trending sub-vertical and steeply N-dipping F2 folds and S2 axial planar foliation (Fig. 1b) strongly affect the Timiskaming Group, constraining the maximum age for D2 at ≤ 2669 Ma (Dimroth et al. 1983; Daigneault et al. 2002; Robert et al. 2005; Bleeker 2015). Pegmatitic dikes associated with the Preissac-LaCorne plutonic suite at ca. 2647 Ma (Feng and Kerrich 1991), ca. 2639 Ma (Ducharme et al. 1997), and ca. 2628 Ma (Davis 2021) cross-cut S2 and provide the minimum age constraint for D2 in the southern Abitibi and the Val-d'Or area. The final deformation period is characterized

by a dextral, NE-trending transpressive strike-slip D3, recognized in mineral stretching lineation along mineralized brittle-ductile reverse shear zones (< 2643 Ma; Robert 1989, 1990, 1994; Wilkinson et al. 1999; Bedeaux et al. 2017; Herzog et al. 2023).

Orogenic gold mineralization in the Val-d'Or vein field

The intermediate to mafic-felsic volcanic and intrusive rocks of the VVF (Figs. 1b and 2) host ~ 46.8 Moz (1460 t) of gold in second to third order reverse shear zones associated with the LLCfz, which contain brittle-ductile, fault-fill shear, and associated extensional quartz-tourmaline-carbonate (QTC) veins (Robert 1989, 1990, 1994; Gosselin and Dubé 2005; Dubé et al. 2007; Monecke et al. 2017; Dubé and Mercier-Langevin 2020). Wallrocks commonly display igneous assemblages composed of varying proportions of plagioclase-quartz-alkalifeldspar-biotite-hornblende-ilmenite-titanomagnetite-magnetite that underwent greenschist-facies metamorphism (Robert 1983; Robert and Brown 1984, 1986a, b; Dubé 2018). These fault-fill, brittle-ductile shear veins dip to the south, strike E-W, and are sub-parallel to oblique to the penetrative S2 foliation that formed towards the peak of the N-S shortening event, syn- to late-D2, at 2643 ± 3 Ma based on compiled xenotime dates (Fig. 2; Herzog et al. 2023). The veins display m-wide, strongly chloritized to quartz-tourmaline-albite-muscovite-pyrite alteration halos. Sulfide mineral assemblages commonly consist of pyrite $\pm$ pyrrhotite $\pm$ chalcopyrite-sphalerite $\pm$ galena and minor late-stage chalcopyrite-sphalerite $\pm$ galena. Gold is hosted dominantly as native Au $\pm$ Ag or Au-Te inclusions in pyrite and as native gold in quartz or tourmaline (Fig. 3, 4, 5; Robert 1983; Robert and Brown 1984, 1986a, b; Robert et al. 2005; Rezeau et al. 2017; Dubé 2018; Daver et al. 2020). A texturally late polymetallic gold-chalcopyrite-carbonate $\pm$ sphalerite $\pm$ galena assemblage is commonly developed in sulfide fractures, which formed at 2607 ± 5 Ma and post-dates the major syn- to late-D2 hydrothermal gold mineralization period (Herzog et al. 2023).

Sampling and analytical techniques

Mine sites, field samples, and petrography

For this study, representative sulfide mineral assemblages from the orogenic gold ores were examined for their relationships with gold-hosting veins and the vein-hosting structural fabric. Five orebodies hosting QTC veins (Goldex, Triangle, Plug #4, Beaufor, Pascalis Gold Trend) were sampled from drill cores. The vein sets, summarized in Table 1, are described in more detail in Herzog et al. (2023). Further

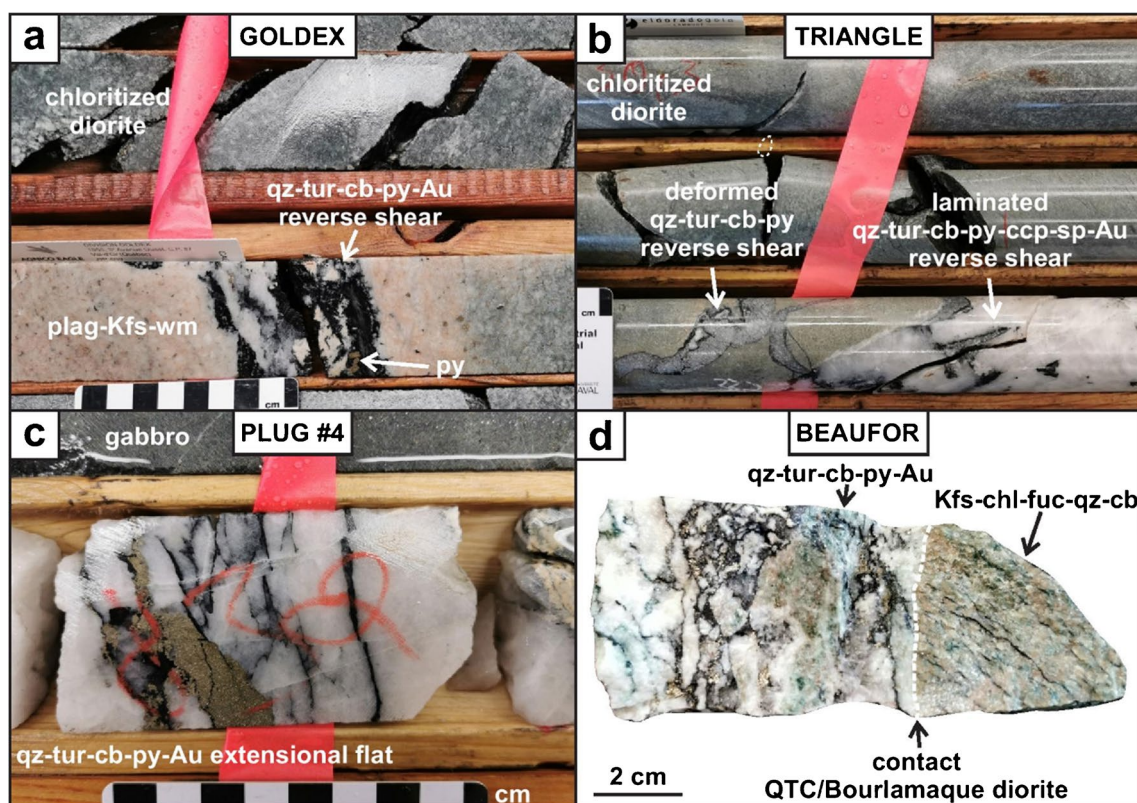


Fig. 3 Field, core, and sample photographs showing key relationships between host rocks and hydrothermal quartz-tourmaline-carbonate veins at **a** Goldex, **b** Triangle, **c** Plug #4, and **d** Beaufor. Cb=carbonate, ccp=chalcopyrite, chl=chlorite, fuc=Cr-bearing phyllo-

silicate, gn=galena, Kfs=K-feldspar, plag=plagioclase, py=pyrite, qz=quartz, sp=sphalerite, tur=tourmaline. QTC=quartz-tourmaline-carbonate vein

material is presented in Electronic Supplementary Materials 1 and 2 (ESM1, Fig. 1; ESM2, Tables 1 and 2). Major sulfide parageneses were established. Detailed characterization of 26 samples by reflected light using a Zeiss Axio Imager M2 was completed to determine the sulfide mineralogy, texture, and paragenesis. Five epoxy mounts were prepared that contained 26 cylindrical rock cores, 6 mm in diameter, which were extracted from characterized samples. The five epoxy mounts were characterized for their major element composition, internal heterogeneity, texture and zonation using energy-dispersive-spectroscopy (EDS), and backscattered electron imaging (BSE) under analytical conditions of 20 kV and 175.9 μ A in a FEI F50 scanning electron microscopy (SEM) at the Laboratoire de Microanalyse (Université Laval).

Sulfide mineral chemistry

The sulfide samples were analyzed at Laboratoire de Microanalyse, for their major and minor element compositions using a CAMECA SX-100 electron probe micro-analyser (EPMA) that is equipped with five wavelength-dispersive spectrometers. The beam size was 10 μ m and beam

conditions at 15 kV and 20 nA. Elements of interest for spot analyses included S, Mn, Fe, Co, Ni, Cu, Zn, Pb, As, and Sb (ESM2, Table 6). A total of 64 spot and line analyses of uncoated sulfide minerals followed using a RESOLUTION 193 nm ArF Excimer laser system (Applied Spectra) equipped with a S-155 large volume ablation cell (Laurin Technic), and coupled to an Agilent 7900 ICPMS, at the LabMaTer (Université du Québec à Chicoutimi). Thirty-four analytes were collected at beam sizes varying between 19 and 55 μ m with a pulse rate of 15 Hz, a scan speed of 10 to 15 μ m/s and a fluence of 3 J/cm². To calculate quantitative sulfide trace element concentrations for line and spot analyses, three reference materials were used as calibrants: Laflamme PO-727 (a synthetic sulfide doped with ~40 μ g/g PGEs, Memorial University), MASS1 (Wilson et al. 2002), and the USGS basaltic glass GSE-1 g (Guillong et al. 2005) using preferred values from the GEOREM database (Jochum et al. 2005) and Fe was used as internal standard based on EPMA analyses. LA-Q-ICPMS data was reduced through Iolite v4 and averaged values (ppm) for each sulfide domain are reported (Table 2; ESM2, Table 3; Woodhead et al. 2007; Paton et al. 2011). Three synthetic sulfides, UQAC-FeS1, UQAC-FeS5 (Savard et al. 2018), and MSS5 (Mungall

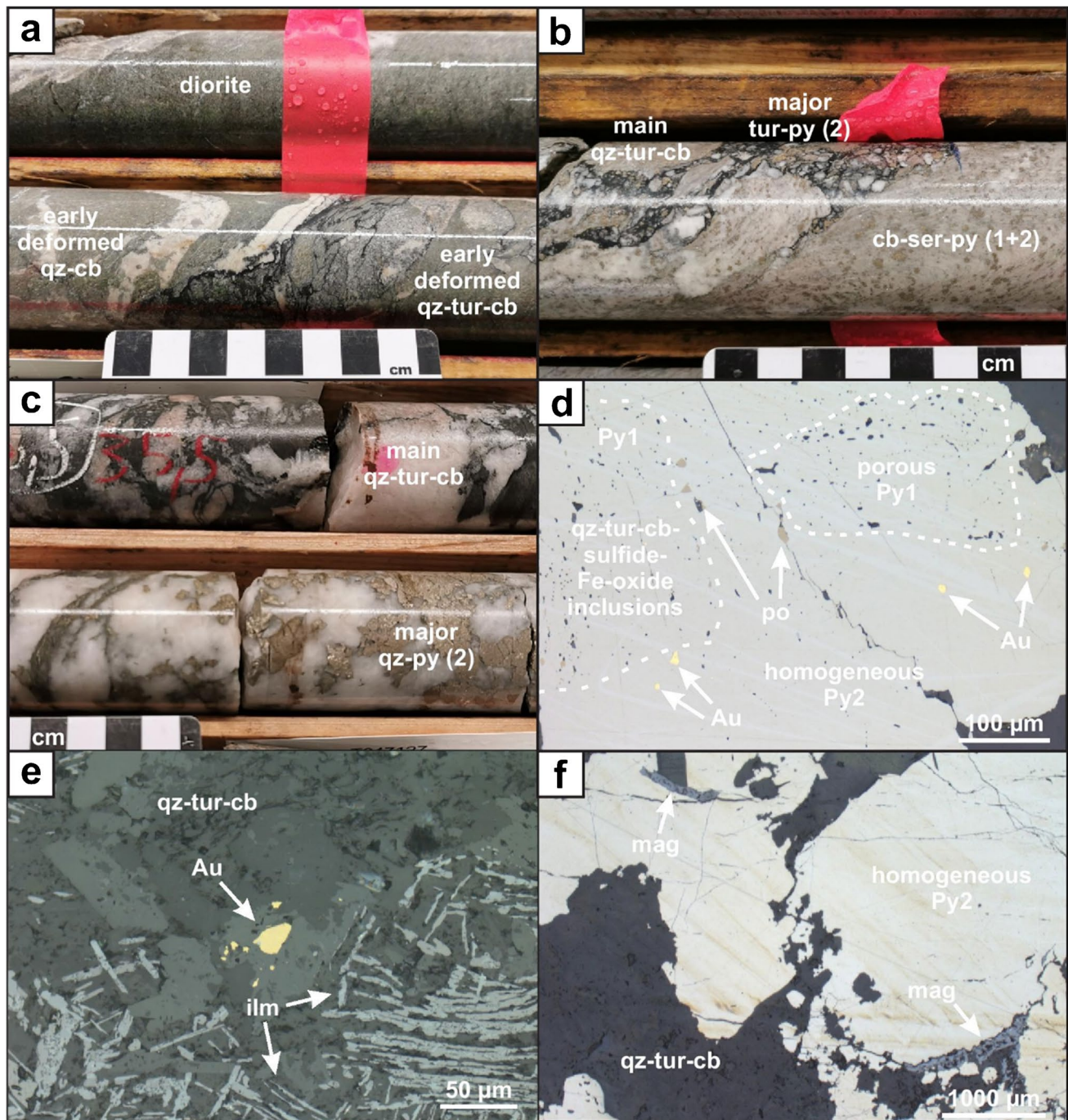


Fig. 4 Common paragenesis of quartz-tourmaline-carbonate veins at the Goldex, Triangle, Plug #4, Pascalis Gold Trend, and Beaufor orebodies, particularly well developed in intrusive host rocks. **a** Early, highly deformed quartz-carbonate veins are commonly cross-cut by a set of deformed, unmineralized quartz-tourmaline-carbonate veins (Triangle). **b** Major gold mineralization hosted in strongly altered wallrock, consisting of primarily carbonate and white mica that host pyrite with a barren, porous Py1 core and Au-bearing, homogeneous Py2 rim (Triangle). **c** Bulk of the gold within brittle-ductile, laminated shear veins is commonly associated with the tourmaline- and

quartz-rich parts of the veins, hosting sulfide aggregates of several cm to dm, primarily composed of pyrite-rich assemblages (Triangle). **d** Porous Py1 core in pyrite, hosting quartz-tourmaline-carbonate as well as sulfide and Fe-oxide inclusions, with a homogeneous Py2 rim overgrowth that contains bulk of the native Au and polymetallic inclusions (Triangle). **e** Native Au associated with ilmenite in quartz-tourmaline-carbonate vein (Plug #4). **f** Homogeneous Py2 rim overgrowth of magnetite (Plug #4). Au=gold, cb=carbonate, ilm=ilmenite, mag=magnetite, qz=quartz, ser=white mica, tur=tourmaline

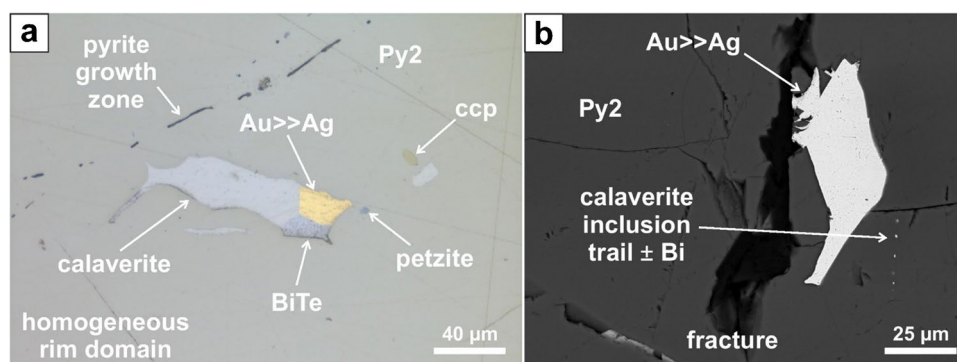


Fig. 5 Polymetallic inclusions (Au–Ag–Te–Bi) with gold in homogeneous Py2 rims, contain calaverite, minor petzite, and various BiTe polytypes with minor base metal sulfides such as chalcopyrite. **a** Reflected light photomicrograph of a typical calaverite-Au ± Ag ± Bi

inclusion in Py2 contained in the Plug #4 orebody. **b** Back-scattered electron image of Py2 from the Goldex orebody containing a trail of small calaverite inclusions and native gold grain

and Brenan 2014), along with GSE-1 g, were also used to assess quality control of the individual laser sessions and are compiled in ESM1, Figs. 6 and 7. In addition to the line and spots, analysis high-resolution quantitative maps of five samples were conducted on selected sulfides grains (ESM1, Figs. 2, 3, 4, and 5). The newly developed method (LA-FF-ICP-TOF-MS) is described in detail in Savard et al. (2023) and Paul et al. (2023) and summarized in ESM1.

Multiple sulfur isotope analyses

In situ multiple sulfur isotope ratios for 91 spots in pyrite (Table 2; ESM2, Table 3) were acquired on a CAMECA IMS1280 Secondary Ion Mass Spectrometer (SIMS), at the Centre for Microscopy, Characterisation and Analysis at the University of Western Australia. The epoxy mount was trimmed at 1 cm and combined with a standard block containing matrix-matched sulfide mineral reference materials including (LaFlamme et al. 2016): Sierra pyrite ($\delta^{33}\text{S} = 1.09 \pm 0.15\text{‰}$; $\delta^{34}\text{S} = 2.17 \pm 0.28\text{‰}$; $\delta^{36}\text{S} = 3.96 \pm 0.60\text{‰}$) and Nifty-b chalcopyrite ($\delta^{33}\text{S} = -1.78 \pm 0.21\text{‰}$; $\delta^{34}\text{S} = -3.58 \pm 0.44\text{‰}$; $\delta^{36}\text{S} = -7.15 \pm 0.63\text{‰}$). The mount was trimmed to a thickness of 4 mm and coated with 30 nm of Au. The sample surface was sputtered over a $5 \times 5 \mu\text{m}$ area with a 10 kV, Gaussian Cs^+ beam with intensity of $\sim 2.5 \text{ nA}$, and total impact energy of 20 kV. Secondary ions were admitted in the double focusing mass spectrometer within a $75 \mu\text{m}$ entrance slit and focused in the center of a $3000 \mu\text{m}$ field aperture ($\times 130$ magnification). Energy was filtered using a 40 eV band pass with a 5 eV gap toward the high-energy side. All sulfur isotopes were collected simultaneously: ^{32}S , ^{33}S , and ^{34}S in Faraday cup detectors fitted with $10^{10} \Omega$ (L2, ^{32}S) and $10^{11} \Omega$ (L1, ^{33}S , and H1, ^{34}S) resistors, and ^{36}S in an electron multiplier (H2), all operating at a mass resolution of ~ 2500 . The $^{32}\text{S}^1\text{H}$ and ^{33}S peaks are not completely resolved under these conditions; thus, the magnetic field was offset slightly to the low-mass side to avoid

interference from $^{32}\text{S}^1\text{H}$ on the ^{33}S peak. The magnetic field was regulated using NMR control. Each analysis includes a pre-sputtering over a $10 \times 10 \mu\text{m}$ area during 30 s, followed by the automatic centering of the secondary ions in the field aperture. Each analysis then consists of a 30 four-second cycles acquisition. Unknown sample material measurements were interspersed with matrix-matched reference material (Sierra pyrite and Nifty-b chalcopyrite). The Sierra pyrite and Nifty-b chalcopyrite were then used to monitor standard repeatability and analytical drift and to correct for instrumental mass fractionation (ESM1). Calculations for the $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ values are compiled in ESM2, Table 4. The average measurement errors (2σ) of the unknowns yield uncertainties for $\delta^{34}\text{S}$ ($\pm 0.30\text{‰}$), $\Delta^{33}\text{S}$ ($\pm 0.20\text{‰}$), and $\Delta^{36}\text{S}$ ($\pm 0.41\text{‰}$). The calculations for the absolute, in situ, propagated errors for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ are outlined in LaFlamme et al. (2016).

High-precision bulk pyrite multiple sulfur isotope analyses (^{32}S , ^{33}S , ^{34}S , and ^{36}S ; $n = 10$) were acquired from QTC veins (ESM2, Table 5) described in Beaudoin and Pitre (2005). The pyrite samples were analyzed at McGill University and analyses followed the multiple sulfur analytical protocol outlined in Helt et al. (2014) and are summarized in ESM1. The analytical uncertainty (1σ) for both, $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values, was $\pm 0.02\text{‰}$.

The $\Delta^{36}\text{S}$ data for in situ and bulk multiple sulfur isotope analyses are reported in ESM2 but not further discussed due to their large absolute errors.

Results

Sulfide paragenesis and relationships of auriferous quartz-tourmaline-carbonate veins

A hydrothermal paragenesis of sulfide and wallrock alteration assemblages was established for each orebody and is

Table 1 Major sulfide mineral parageneses and associated sulfide mineral textures recorded in each orebody

Mineralization style	Orebody	Relative sulfide paragenesis	Sulfide texture	Mineral assemblage
Quartz-tourmaline-carbonate vein	Goldex	Py1a	Anhedral, homogeneous to minor heterogeneous zones, strongly fractured, irregular rim, no inclusions	qz-tur-cb-py-ccp
		Py1b	Euhedral, eroded rim, homogeneous, porous core, and homogeneous rim, tur-cb inclusions	qz-tur-cb-py-Au
		Py2	Euhedral, weakly irregular rim, weakly fractured, rt inclusions, sub-parallel to foliation	qz-cb-py-rt
	Triangle	Py1	Euhedral, homogeneous silicate inclusions, weakly eroded rim, weakly fractured, replaced by Py2 and forms porous core	qz-cb-py-ccp
		Py2	Sub-euhedral, homogeneous to minor heterogeneous zonation, strongly fractured, strongly eroded rim, porous core, cb-tur inclusions	qz-tur-cb-py-ccp-po-sch-rt-Au
		Ccp3	Anhedral, homogeneous, hosted in Py1 and Py2 fractures	qz-cb-ccp
	Plug #4	Py1	Euhedral, homogeneous silicate inclusions, weakly eroded rim, weakly fractured, replaced by Py2 and forms porous core	qz-cb-py-ccp-sch-mt-po
		Py2	Sub-euhedral, homogeneous to minor heterogeneous zonation, strongly fractured, strongly eroded rim, porous core, cb-tur inclusions	qz-tur-cb-py-ccp-po-sch-rt-tellurides Au
		Ccp3	Anhedral, homogeneous, hosted in Py1 and Py2 fractures	qz-cb-ccp
	Pascal's Gold Trend	Py1	Euhedral, homogeneous, minor porous core, weakly eroded rim, weakly fractured, ccp inclusions, replaced by Py2	qz-tur-cb-py-po-ccp-mag
		Py2	An-sub-euhedral, homogeneous, porous core, weakly to strongly fractured, strongly eroded rim, cb-tur-ccp inclusions, replaced by Ccp3	qz-tur-cb-py-po-Au
		Ccp3	Subhedral, homogeneous, strongly eroded rim, weakly fractured, hosted in Py1 & Py2 fractures and rims	cb-qz-py-ccp-rt
	Beaufor	Py1	Anhedral, homogeneous, silicate-cb inclusions, strongly eroded rim, strongly fractured	qz-chl-py-ccp-mol
		Py2	An-subhedral, homogeneous to minor heterogeneous zonation, strongly fractured, strongly eroded rim, cb-tur-ccp inclusions	qz-tur-cal-ank-dol-py-po-ccp-sch-Au-tellurides
		Ccp3	Minor, anhedral, homogeneous, hosted in Py1 and Py2 fractures	qz-cb-ccp

Ab = albite, *Ag* = silver, *ank* = ankerite, *Au* = gold, *bt* = biotite, *bn* = bornite, *cal* = calcite, *cb* = carbonate, *ccp* = chalcopyrite, *chl* = chlorite, *dol* = dolomite, *ep* = epidote, *gn* = galena, *hem* = hematite, *mag* = magnetite, *mol* = molybdenite, *po* = pyrrhotite, *py* = pyrite, *qz* = quartz, *rt* = rutile, *sch* = scheelite, *sp* = sphalerite, *tur* = tourmaline

summarized in Figs. 3 and 4. More detailed descriptions of sulfide mineral textures are in Table 1 as well as in ESM2, Tables 1 and 2.

The Goldex, Triangle, Plug #4, Pascal's Gold Trend, and Beaufor orebodies host gold in association with QTC veins (Fig. 4a), which contain pyrite-rich sulfide assemblages

(> 95 vol%) within cm- to dm-sized pyrite aggregates. These pyrite aggregates can form within the laminated vein or occur within altered wallrock, particularly in “sericitized” or tourmalinized areas (Figs. 3a–d and 4b–c). Vein alteration halo assemblages include pervasive quartz- “sericite”-albite-chlorite-carbonate and minor Cr-bearing phyllosilicates

Table 2 Summary of in situ multiple sulfur isotopic and trace element compositions (detection limit < 100 ppb) recorded in pyrite (Py1, Py1a, Py1b, Py2), and bulk pyrite multiple sulfur isotopic compositions

Orebody	Relative sulfide paragenesis	$\delta^{34}\text{S}$ (‰) MIN	2σ	$\delta^{34}\text{S}$ (‰) MAX	2σ	$\Delta^{33}\text{S}$ (‰) MIN	2σ	$\Delta^{33}\text{S}$ (‰) MAX	2σ	Co (ppm)	Ni (ppm)	As (ppm)	Se (ppm)	Sb (ppm)	Te (ppm)	Bi (ppm)	Au (ppm)	Ag (ppm)
Goldex	Py1a+b	-0.4	0.3	0.4	0.3	-0.13	0.07	-0.02	0.05	424	635	33	6	n.d	8	8	30	2
	Py2	0.0	0.3	2.4	0.3	-0.15	0.11	0.01	0.11	1450	1700	125	220	100	145	230	1250	5
	Bulk			0.2	0.04			-0.03	0.04									
Triangle	Py1	0.0	0.3	3.5	0.3	-0.03	0.11	0.23	0.10	2000	463	16	50	15	5	15	n.d	3
	Py2	2.5	0.3	4.3	0.3	-0.16	0.10	-0.01	0.11	529	300	541	75	35	75	50	115	25
Plug #4	Py1	2.2	0.3	3.4	0.3	-0.20	0.10	-0.08	0.10	128	22	9	4	n.d	22	5	11	17
	Py2	3.1	0.3	4.6	0.3	-0.15	0.10	-0.03	0.11	401	26	148	897	1	1110	1120	160	71
Pascalis	Py1	4.9	0.3	5.2	0.3	-0.05	0.05	0.01	0.05	4500	520	100	n.d	25	40	50	n.d	10
Gold Trend	Py2	3.5	0.3	5.2	0.3	-0.16	0.05	-0.03	0.05	8000	550	550	550	40	2250	3000	165	205
	Bulk			4.2	0.04			-0.03	0.04									
Beaufor	Py1	5.6	0.3	5.8	0.3	-0.12	0.11	-0.04	0.11	389	493	67	47	n.d	6	6	n.d	n.d
	Py2	5.9	0.3	6.3	0.3	-0.13	0.11	0.00	0.11	503	437	199	48	n.d	12	21	n.d	n.d
	Bulk			5.0	0.04			-0.01	0.04									
Louvi-court	Bulk			1.3	0.04			-0.03	0.04									
Gold-fields																		
Buffadison	Bulk			4.9	0.04			-0.04	0.04									
Sleepy Lake	Bulk			1.5	0.04			-0.07	0.04									
Wrightbar	Bulk			5.9	0.04			-0.01	0.04									
Nubell	Bulk			2.1	0.04			-0.06	0.04									
Canmet	Bulk			5.3	0.04			0.00	0.04									
Siscoe	Bulk			4.5	0.04			-0.05	0.04									

n.d. = below detection limit, *Py* = pyrite

(Fig. 3d). Pyrite commonly shows a porous core (Py1) with abundant carbonate, tourmaline and minor sulfides, including chalcopyrite, sphalerite, galena, and pyrrhotite as well as Fe-Ti-oxides such as ilmenite, titanomagnetite, and magnetite (Fig. 4d–f) and a homogeneous pyrite rim (Py2). Inclusion size and distribution of Py1 from veins strongly contrasts with that in wallrocks. Vein-hosted pyrite (Fig. 4d) shows erratically distributed, larger inclusion sizes up to hundreds of μm in size, whereas wallrock-hosted pyrite contains evenly distributed, smaller sized inclusions. The homogeneous Py2 rim hosts native Au and polymetallic Au–Ag–Te–Bi inclusions, primarily calaverite, which range from nm to μm in size (Fig. 5a–b). Both pyrite cores (Py1) and rims (Py2) are cross-cut by micro-fractures, which typically contain a chalcopyrite-carbonate–Au–Ag–Te–Bi $\pm$ sphalerite $\pm$ galena assemblage. At Goldex, the early Py1 can be divided into Py1a, which displays an anhedral texture and is fractured and inclusion-free. Py1b is euhedral with an irregular rim that commonly contains silicate, tourmaline, and carbonate, as well as rare native gold, inclusions. Py1b forms the porous core for Py2.

Sulfide mineral compositions

In situ elemental analyses of chalcopyrite and pyrite from vein and alteration mineral assemblages at the Goldex, Triangle, Plug #4, Pascalis Gold Trend and Beaufor orebodies reveal that out of 34 measured analytes, only the elements Au, Ag, Te, Bi, Co, Ni, As, Se, and Sb (Table 2; ESM2, Table 3) occur above detection limits (< 100 ppb) as minor ($< 10,000$ ppm) and trace concentrations (< 1000 ppm) in Py1 cores and Py2 rims. Only Py1b (Au ≤ 30 ppm) and Py1 (Au ≤ 11 ppm) cores hosted in Goldex and Plug #4, respectively, contain trace concentrations of Au. In general, Py2 rims contain the bulk of the gold as native gold or polymetallic gold inclusions (Fig. 6), which include major calaverite and minor petzite, with other Au–Ag–Bi–Te assemblages of various compositions (Au ≤ 1250 ppm; Ag ≤ 205 ppm; Te ≤ 2250 ppm; Bi ≤ 3000 ppm).

Goldex pyrite yields lower concentrations of Co (≤ 424 ppm) and Ni (≤ 635 ppm) in porous Py1a and Py1b (Table 2) compared to oscillatory zoned Co, Ni, and As in Py2 (Co ≤ 1450 ppm; Ni ≤ 1700 ppm; As ≤ 125 ppm). Homogeneous Py2 also contains areas of relatively high Se and Sb (both ≤ 220 ppm) concentrations. Gold occurs at low concentrations in Py1b (≤ 30 ppm) and within nanometer-sized polymetallic gold inclusions contained in Py2 (Fig. 5b).

Triangle pyrite displays locally distributed areas of Co (≤ 2000 ppm), Ni (≤ 400 ppm), and Se (≤ 50 ppm) in porous Py1 (Table 2) and low concentrations of Co (≤ 529 ppm), as well as oscillatory zoned Ni (≤ 300 ppm) and As (≤ 541 ppm) associated with homogeneous Py2. Visible

polymetallic inclusions and sporadic distribution of Sb (≤ 35 ppm) characterizes Py2.

Pyrite from Plug #4 yields primarily low concentrations of Co (≤ 128 ppm) and Ni (≤ 22 ppm) in porous Py1 and Py2 (Co ≤ 401 ppm; Ni ≤ 26 ppm), the latter of which also shows enrichment in As (≤ 148 ppm) and Se (≤ 897 ppm). Low concentrations of Au (≤ 11 ppm), Ag (≤ 17 ppm), Te (≤ 22 ppm), and Bi (≤ 5 ppm) occur in Py1, but no inclusions were observed. Py2 contains gold in visible polymetallic inclusions (Fig. 5a).

Porous Py1 from the Pascalis Gold Trend (Table 2) yields localized areas of minor concentrations in Co (≤ 4500 ppm) and Ni (≤ 550 ppm). Homogeneous Py2 shows oscillatory zones in Co (≤ 3300 ppm), Ni (≤ 2200 ppm), and As (≤ 550 ppm). One analyzed Py2 rim has the highest recorded concentration of Co (Fig. 6; Co ≤ 8000 ppm) in all orebodies. Elevated concentrations of Co, Ni, and As (Fig. 6) in oscillatory zoned Py2 appear unrelated to inclusions.

Porous Beaufor Py1 primarily contains low trace concentrations of Co (≤ 389 ppm) and Ni (≤ 493 ppm). Homogeneous Py2 contains low Co (≤ 503 ppm) and Ni (≤ 437 ppm), but higher local concentrations of As (≤ 199 ppm), Se (≤ 48 ppm), and negligible Sb.

Multiple sulfur isotope composition

In situ multiple sulfur isotopic composition of pyrite ($n=91$) from QTC veins at Goldex, Triangle, Plug #4, Pascalis Gold Trend, and Beaufor orebodies (Fig. 7a; ESM2, Table 3) shows a moderate range in $\delta^{34}\text{S}$ (from -0.4‰ to 6.3‰ ; Fig. 7b) and a narrow range in $\Delta^{33}\text{S}$ values (from -0.20‰ to 0.23‰ ; Fig. 7c). Pyrite commonly yields a shift in $\delta^{34}\text{S}$ values ($< 3.0\text{‰}$), from Py1 cores to Py2 rims (Figs. 7a and 8; Table 2). Similarly, bulk pyrite multiple sulfur isotope analyses (Fig. 7a; Table 2) yield $\delta^{34}\text{S}$ values from 0.6‰ to 6.0‰ and $\Delta^{33}\text{S}$ from -0.07‰ to 0‰ . Both, in situ and bulk pyrite multiple sulfur isotope data, have a similar range in sulfur isotopic compositions, with a systematically small, mostly negative deviation in $\Delta^{33}\text{S}$, outside the field for mass-dependent fractionation of sulfur (MDF-S). The analytical uncertainty (2σ) for negative $\Delta^{33}\text{S}$ values overlaps with the MDF-S field, such that care must be exercised in interpretation.

Sulfur isotope analyses of pyrite ($n=29$) from the Goldex orebody show the lowest $\delta^{34}\text{S}$ values (-0.4‰ to 0.5‰) that are associated with the barren Py1a and Py1b core domains (Fig. 8c). Higher $\delta^{34}\text{S}$ values (0.0‰ to 2.4‰) characterize Py2 rims (Fig. 7a; Table 2). Both pyrite domains yield a consistent negative $\Delta^{33}\text{S}$ range between -0.15‰ and 0.01‰ .

Py1 core hosted in altered diorite wallrock of the Triangle orebody (Fig. 8a) records a $\delta^{34}\text{S}$ value of -0.1‰ (Fig. 7a) and the highest $\Delta^{33}\text{S}$ value (0.23‰) of all QTC orebodies and in general range between 0.6‰ and 3.5‰ , with $\Delta^{33}\text{S}$

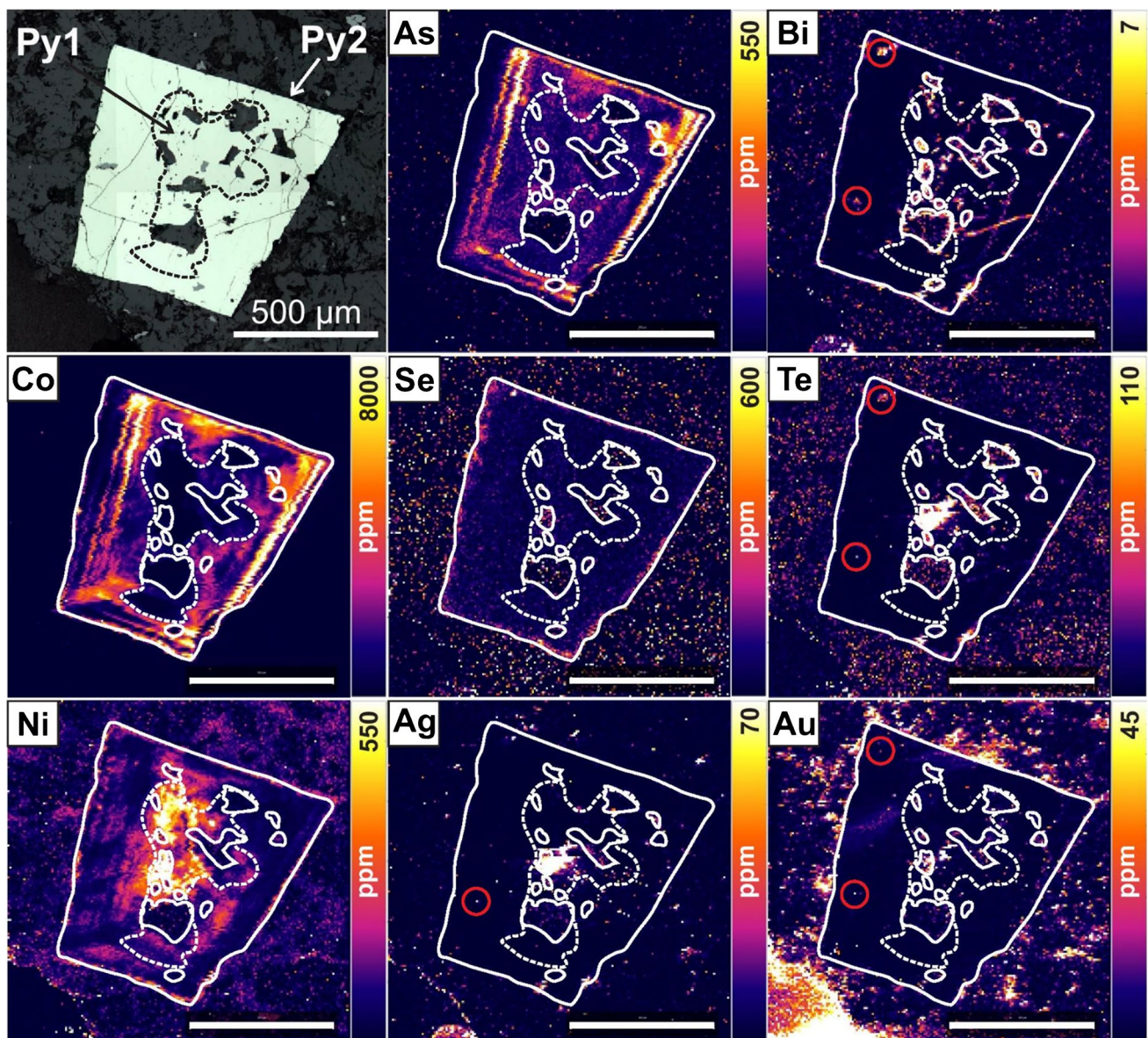


Fig. 6 Reflected light photomicrograph, qualitative, and quantitative LA-FF-ICP-TOF-MS maps of Py1 and Py2 from Pascalis Gold Trend (PGT_34), showing the key minor and trace elements As, Bi, Co, Se,

Te, Ni, Ag, and Au in the quartz-tourmaline-carbonate veins. Red circles indicate areas hosting polymetallic inclusions (Au-Ag-Te-Bi)

values between -0.03‰ and 0.11‰ ($n=9$). This single outlier could also be explained if a Py1 inclusion was measured during in-situ sulfur isotope analysis. The Py2 rim shows higher $\delta^{34}\text{S}$ values (up to 4.3‰) and negative $\Delta^{33}\text{S}$ values ($>-0.16\text{‰}$). Higher $\delta^{34}\text{S}$ and negative $\Delta^{33}\text{S}$ values commonly characterize vein-hosted Py2 ($n=16$; Fig. 7a; Table 2).

Vein pyrites from Plug #4 ($n=14$) show lower $\delta^{34}\text{S}$ values recorded in Py1 cores (2.2‰) compared to higher values in Py2 rims (up to 4.6‰). Both pyrite domains display a small negative $\Delta^{33}\text{S}$ range between -0.20‰ and -0.03‰ (Fig. 7a; Table 2).

Pyrite domains Py1 and Py2 from the Pascalis Gold Trend orebody ($n=14$) display a narrow range in $\delta^{34}\text{S}$ values, between 5.2‰ and 3.5‰ , respectively (Fig. 7b), and $\Delta^{33}\text{S}$ values range between -0.16‰ and 0.01‰ (Fig. 7a; Table 2).

Vein pyrites at Beaufor ($n=9$) display lower $\delta^{34}\text{S}$ values in Py1 core ($>5.6\text{‰}$) and higher $\delta^{34}\text{S}$ values in the Py2 rim ($<6.3\text{‰}$). Both pyrite domains show negative $\Delta^{33}\text{S}$ values ($>-0.13\text{‰}$; Fig. 7a; Table 2).

Bulk pyrite multiple sulfur data from vein pyrite samples (Table 2; ESM2, Table 5; $n=10$) described in Beaufoin and Pitre (2005) yield a similar range in $\delta^{34}\text{S}$ values

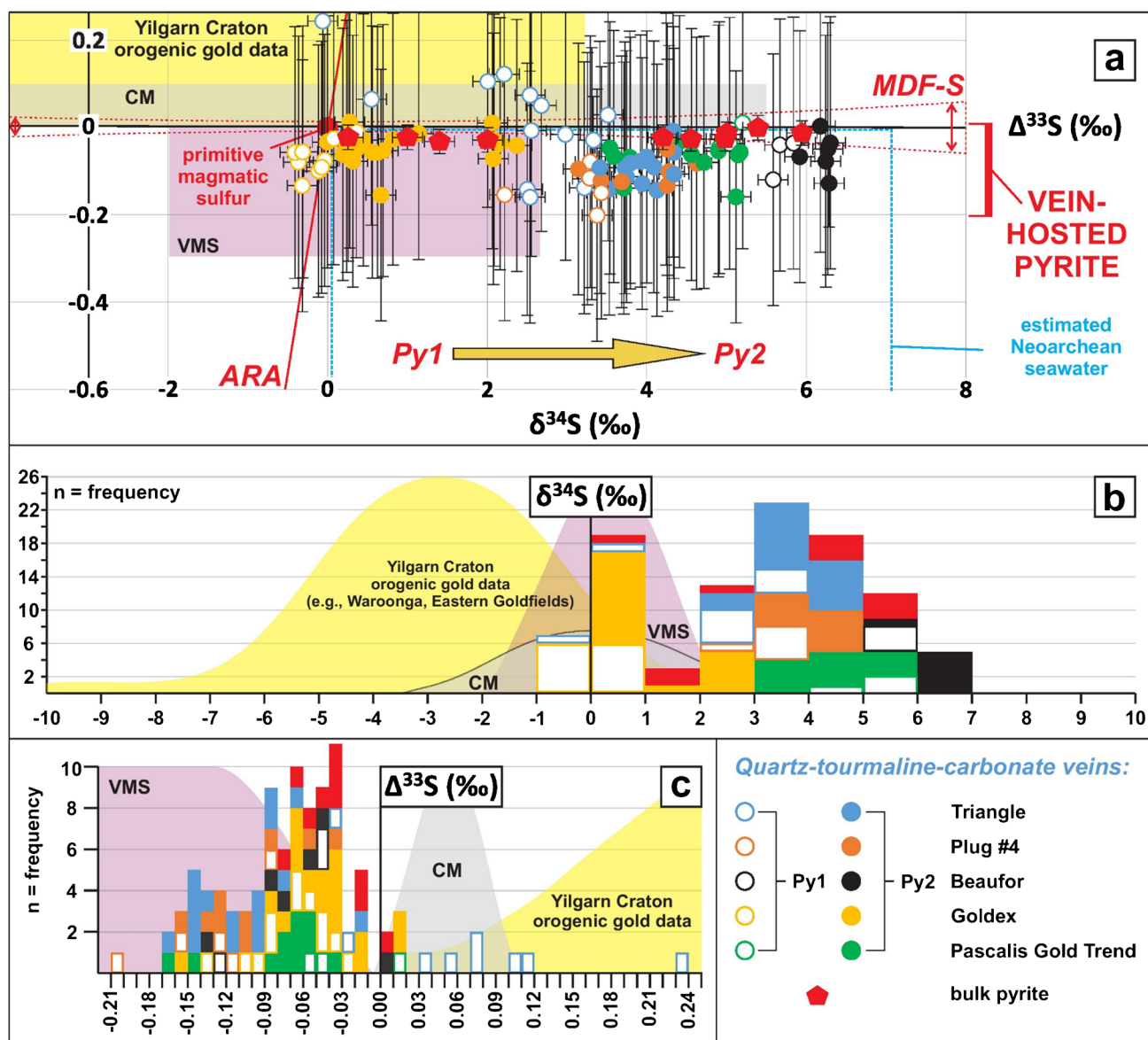


Fig. 7 **a** A $\delta^{34}\text{S}$ vs. $\Delta^{33}\text{S}$ plot showing multiple sulfur isotope data (pyrite) for Py1 and Py2 associated with quartz-tourmaline-carbonate veins (Triangle, Plug #4, Beaufor, Goldex, Pascalis Gold Trend) and alteration halos (Triangle) from the VVF. Outline of the mass-dependent fractionation field for sulfur (MDF-S, LaFlamme et al. 2018b). Error bars (2σ) display the overall analytical uncertainties. All individual SIMS spot and bulk pyrite analyses are in Table 2 and ESM 2. Bulk multiple sulfur isotope data for Canadian Malartic (CM, Helt 2012; Helt et al. 2014), volcanogenic massive sulfide deposits (VMS, Sharman et al. 2015) of the Abitibi subprovince, as well as primitive magmatic sulfur with a composition of $\delta^{34}\text{S}=0\text{‰}$ and

$\Delta^{33}\text{S}=0\text{‰}$ (Labidi et al. 2013; Fiorentini et al. 2018) and the estimated range of Neoproterozoic seawater yielding values of $\delta^{34}\text{S}>0\text{‰}$ and $\Delta^{33}\text{S}<-1.5\text{‰}$ (Jamieson et al. 2013). **a** A $\delta^{34}\text{S}$ vs. $\Delta^{33}\text{S}$ plot for both pyrite generations hosted within quartz-tourmaline-carbonate veins. The golden arrow indicates observed sulfur isotope evolution trends from porous Py1 cores towards homogeneous Py2 rims. ARA=Archean Reference Array of $\Delta^{33}\text{S} \approx 0.89 \times \delta^{34}\text{S}$ (Ono et al. 2009). Bulk and in situ multiple sulfur isotope data from orogenic gold deposits hosted in the Yilgarn Craton compiled in LaFlamme et al. (2018c). **b** Frequency plot of $\delta^{34}\text{S}$ values for each orebody. **c** Frequency plot of $\Delta^{33}\text{S}$ values for each orebody

(between 0.2‰ and 5.9‰) and a narrow range in $\Delta^{33}\text{S}$ values (between -0.07‰ and 0‰). Pyrite from Goldex, Lucien-Béliveau (extension of the Pascalis Gold Trend),

and Beaufor have bulk $\delta^{34}\text{S}$ (0.2‰ , 4.2‰ , and 5.0‰ , respectively) and $\Delta^{33}\text{S}$ (-0.03‰ , -0.03‰ , and -0.01‰ ,

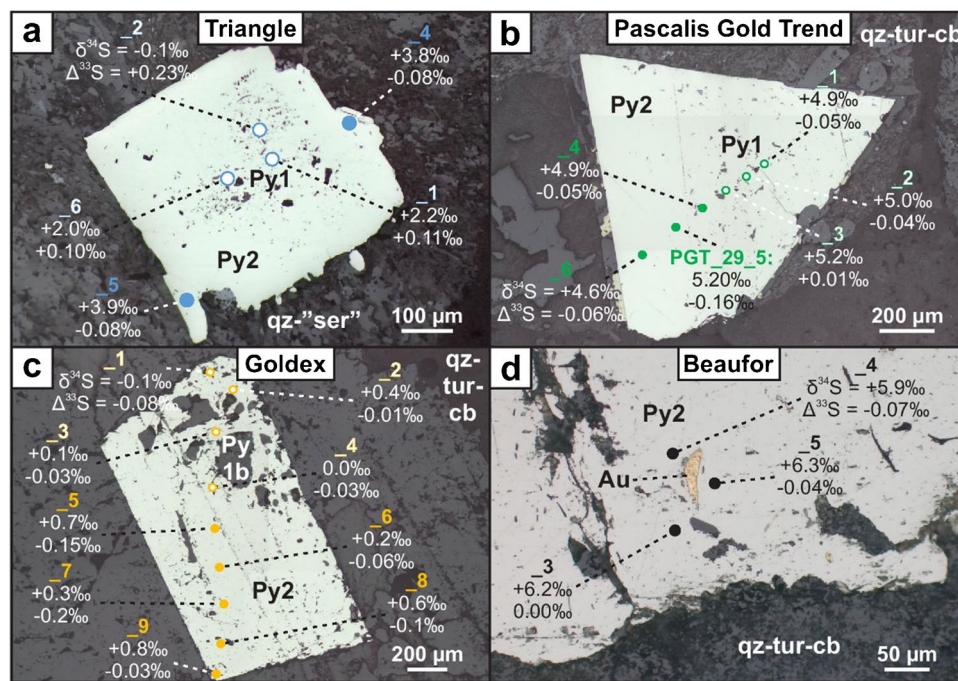


Fig. 8 Reflected light photomicrographs showing key sulfide mineral assemblages and in-situ SIMS analyses. Empty symbols represent texturally early Py1 and filled symbols texturally late Py2 associated with native Au inclusions. **a** Pyrite hosted in altered quartz-sericite alteration halo at the Triangle orebody. Early, porous Py1 core with abundant silicate inclusions shows slightly lower $\delta^{34}\text{S}$ and significantly higher $\Delta^{33}\text{S}$ values compared to the homogeneous Py2 rim that hosts polymetallic inclusions (2σ : $\delta^{34}\text{S} < 0.3\text{‰}$ and $\Delta^{33}\text{S} < 0.10\text{‰}$; analysis number LQ_20_x). **b** Pyrite hosted in quartz-tourmaline-carbonate vein at Pascalis Gold Trend, showing porous Py1 core and

homogeneous Py2 rim. Both domains have a narrow range in $\delta^{34}\text{S}$ and negative $\Delta^{33}\text{S}$ signature (2σ : $\delta^{34}\text{S} < 0.3\text{‰}$ and $\Delta^{33}\text{S} < 0.05\text{‰}$; analysis number PGT_29_x). **c** Early, porous pyrite core contains large tourmaline and carbonate inclusions, shows slightly lower $\delta^{34}\text{S}$ values compared to the rim at Goldex. Both domains yield slightly negative $\Delta^{33}\text{S}$ values (2σ : $\delta^{34}\text{S} < 0.3\text{‰}$ and $\Delta^{33}\text{S} < 0.11\text{‰}$; analysis number GX_35_x). **d** Homogeneous Py2 rim in a quartz-tourmaline-carbonate vein of the Beaufor orebody, which hosts a native Au inclusion and shows slightly higher $\delta^{34}\text{S}$ and negative $\Delta^{33}\text{S}$ values (2σ : $\delta^{34}\text{S} < 0.3\text{‰}$ and $\Delta^{33}\text{S} < 0.11\text{‰}$; analysis number LB_C481_26R_x)

respectively) values within the range recorded in Py1 and Py2 by in situ multiple sulfur analyses (Fig. 7a–c).

Discussion

Most commonly proposed fluid mechanisms associated with sulfide and gold precipitation in orogenic gold systems include fluid mixing (e.g., Cameron and Hattori 1987; Beaudoin and Pitre 2005; Neumayr et al. 2008; Beaudoin and Chiaradia 2016), fluid boiling and immiscibility (Peterson and Mavrogenes 2014; Sugiono et al. 2022), and fluid-rock reactions (Phillips 1986; Ward et al. 2017). Orogenic gold systems in meta-sedimentary rock successions commonly incorporate Au as “invisible gold” through coupled Au-As redox reactions into As-rich sulfides (e.g., Pokrovski et al. 2019, 2021), whereas in meta-volcanic rocks, gold frequently occurs in the form of polymetallic (Au-Ag-Te-Bi) inclusions in As-poor sulfides, suggesting different fluid mechanisms to precipitate gold (e.g., Bi et al. 2011; Sherlock et al. 2012). These processes have an important bearing on $f\text{O}_2$ and/or $f\text{S}_2$ conditions of a hydrothermal fluid and

accordingly gold solubility that control the style of orogenic gold deposits. Here, we examine the within-grain sulfide multiple sulfur isotope and trace element signatures to better understand hydrothermal fluid mechanisms that precipitate Au-Ag-Te-Bi-bearing sulfides in orogenic gold deposits.

Gold-hosting pyrite and auriferous hydrothermal fluid signatures

The VVF includes several QTC vein orebodies including Goldex, Triangle, Plug #4, Pascalis Gold Trend, and Beaufor that are hosted in meta-volcanic and intrusive rocks (Fig. 3). These veins commonly display at least two texturally and chemically distinct sulfide generations (Table 2): a porous silicate, carbonate and minor sulfide, and Fe-oxide inclusion-bearing Py1 core, which is surrounded by a homogeneous Py2 rim (Fig. 4). The Py2 rim hosts most of the gold, either as native or polymetallic Au-Ag-Bi-Te inclusions (Fig. 5; e.g., Robert 1983; Robert and Brown 1984, 1986b; Rezeau et al. 2017; Daver et al. 2020). Robert and Brown (1986b) and Rezeau et al. (2017) recognized the precipitation of texturally late pyrrhotite at Sigma and Lac Herbin (Fig. 1b)

associated with the late stages of QTC vein formation, which coincides with the precipitation of Py2. This association of late homogeneous Py2 rims and pyrrhotite, and the lack of abundant hematite or acidic alteration halos (Figs. 3 and 4), imply that the pyrite-rich assemblages formed under reducing fluid fO_2 and near-neutral pH conditions, within the pyrite stability field (Figs. 8, 9a).

The textural relationship between a porous pyrite core (Py1) surrounded by a homogeneous pyrite rim (Py2) is frequently documented in orogenic gold systems and interpreted to record coupled dissolution-reprecipitation reactions in sulfide minerals (e.g., McCuaig and Kerrich 1998; Goldfarb et al. 2001, 2005; Robert et al. 2005; Fougereuse et al. 2016). In many cases, pyrite dissolution and remobilization require interaction with a high fO_2 and low pH (<5) hydrothermal fluid and an increase in fluid fS_2 during the reaction, which will lead to reprecipitation of marcasite (Fougereuse et al. 2016; Wu et al. 2019). However, marcasite is not recorded in pyrite of the VVF. The erratically distributed, large-sized inclusions recorded in Py1 (Figs. 4d, 6 and 8b–d), the low variability in trace element compositions (Fig. 6), and consistent $\Delta^{34}S$ signatures between Py1 and Py2 suggest that Py2, which overgrows Py1 and gangue minerals, was precipitated from an evolved hydrothermal fluid.

In the five investigated orebodies, Py2 hosts most of the gold primarily in the form of polymetallic inclusions composed of calaverite and native gold with minor petzite. However, polymetallic inclusions that lack major Au-bearing tellurides can contain various proportions of Au (≤ 1250 ppm), Ag (≤ 205 ppm), Te (≤ 2250 ppm), and Bi (≤ 3000 ppm). In Goldex (Py1b) and Plug #4 (Py1), low concentrations of lattice-bound Au could be identified (≤ 30 ppm). Daver et al. (2020) noted pyrite rims and cores that contain similarly low concentrations for Ni (≤ 4000 ppm), Co (≤ 700 ppm), and As (≤ 100 ppm) in pyrite from the Lac Herbin, Goldex, Beaufor, and Triangle orebodies (Fig. 1b). Moreover, it has been shown that As contents higher than 1000 ppm in pyrite facilitate the uptake of lattice-bound gold into pyrite through Au-As coupled redox reactions (Reich et al. 2005; Pokrovski et al. 2019, 2021; Wu et al. 2021). The low As contents recorded in Py1, Py1b (≤ 67 ppm), or Py2 (≤ 550 ppm) may, therefore, explain the formation of gold-bearing inclusions and nm- to μ m-sized polymetallic inclusion trails within crystal lattice deficiencies developed during pyrite growth (Figs. 5 and 10a).

Multiple sulfur isotope signature of hydrothermal fluid

The $\delta^{34}S$ values for Py1 cores and Py2 rims (Table 2) from the five orebodies are as follows: Goldex = -0.4‰ to 2.4‰ ; Triangle = 0.0‰ to 4.3‰ ; Plug #4 = 2.2‰ to 4.6‰ ; Pascalis Gold Trend = 4.9‰ to 5.2‰ ; and Beaufor = 5.6‰ to 6.3‰ . Mean $\Delta^{34}S$ values (Table 3) are $-0.03 \pm 0.17\text{‰}$

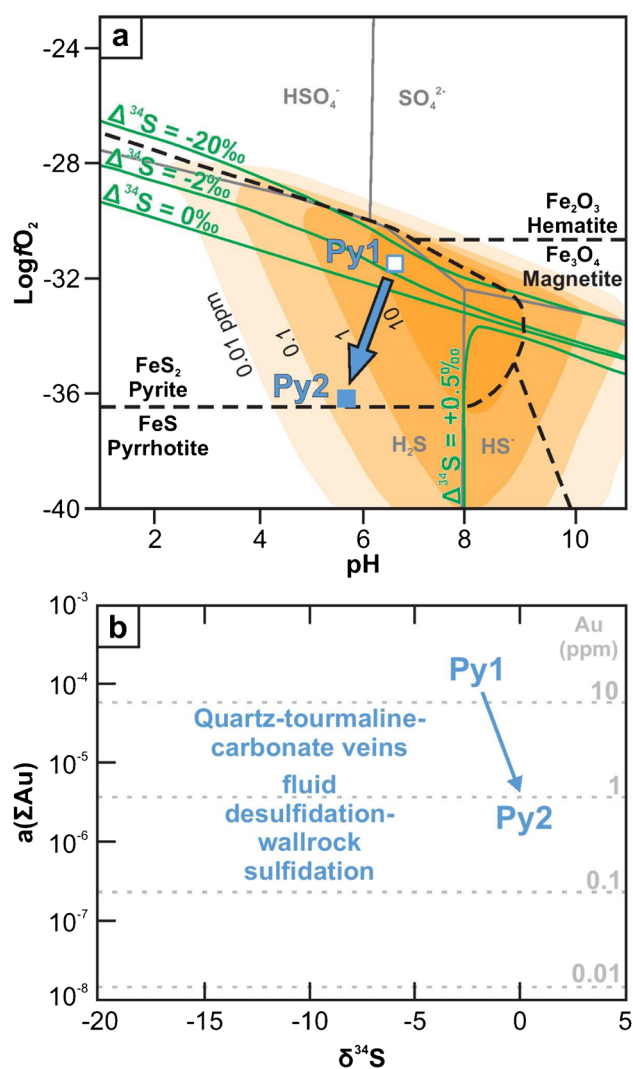


Fig. 9 **a** A fO_2 -pH diagram showing characteristic fluid conditions for orogenic gold mineralization. The blue arrow represents the hydrothermal fluid paths leading to gold deposition in quartz-tourmaline-carbonate veins of the VVF. Modified after Ohmoto (1972) and Hodkiewicz et al. (2009). The mineral stability fields of the Fe-O-S system and sulfur species are based on $\Sigma S = 0.05$ mol/kg, and solid green lines ($\Delta^{34}S$) represent contour lines of isotopic shifts in $\delta^{34}S$ values. Gold solubility contour lines (in ppm) are taken from Shenberger and Barnes (1989). Further experimental conditions include $T = 300$ °C, $P = 1$ kbar, $Na^+ = 1$ m, $K^+ = 0.1$ m, $Ca^{2+} = 0.01$ m, and $\Sigma \delta^{34}S = 0\text{‰}$. **b** Activity diagram showing the relationships between changes in $\delta^{34}S$, related to the removal of H_2S from a hydrothermal fluid, and total gold solubility ($a(\Sigma Au)$) and the observed hydrothermal processes associated with gold precipitation in the quartz-tourmaline-carbonate veins. Modified after Palin and Xu (2000)

(2SD) for Py1 and $-0.08 \pm 0.09\text{‰}$ (2SD) for Py2. This negative $\Delta^{34}S$ signature (ranging from -0.20‰ to 0.01‰) in pyrite-rich veins of the VVF (Fig. 7a–c) must be treated with caution due to single spot uncertainties within error of 0‰ and overlap with the MDF-S field (Fig. 7a). Even

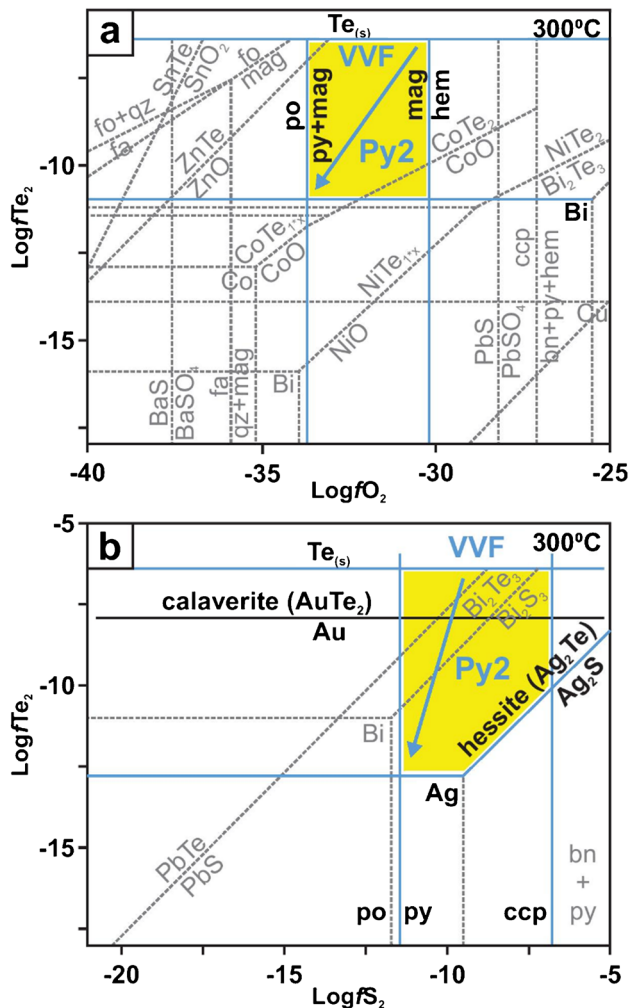


Fig. 10 **a** Diagram showing Au and As contents of Py1 and Py2 in log Au (mol%) vs. log As (mol%) space to determine gold solubility as a function of As-contents in pyrite. Modified from Reich et al. (2005) and Pokrovski et al. (2019). **b** A log f_{Te_2} -log f_{S_2} diagram showing the formation of increasingly Ag-rich tellurides during f_{S_2} decrease and Py2 growth, at conditions of $T=300\text{ }^{\circ}\text{C}$, $P=1\text{ bar}$. Modified from Afifi et al. (1988a). Bn=bornite; ccp=chalcopyrite; po=pyrrhotite; py=pyrite; VVF=Val-d’Or Vein Field

if systematic, the negative $\Delta^{33}\text{S}$ signature could represent an apparent trend, which can result from SIMS drift correction, known to cause a variation of $\pm 0.1\text{‰}$ (Whitehouse 2013). Nonetheless, a similarly small and negative trend in bulk pyrite multiple sulfur data (Fig. 7a–c; Table 2; ESM2, Table 5) is consistent with the in-situ SIMS $\Delta^{33}\text{S}$ values in the VVF.

The small negative range in $\Delta^{33}\text{S}$ values is in contrast with bulk pyrite multiple sulfur isotope data by Helt (2012), reporting primarily positive $\Delta^{33}\text{S}$ values, ranging from -0.01‰ to 0.11‰ , at the Pontiac sedimentary rock-hosted Canadian Malartic deposit (Fig. 7a). Similarly, orogenic gold districts in the Yilgarn Craton commonly yield

Table 3 Overview of recorded mean, in situ, multiple sulfur isotopic, and sulfide trace element compositions recorded in relative sulfide paragenesis

Sulfide	Relative sulfide paragenesis	$\delta^{34}\text{S}$ (‰)	MEAN	2SD	$\Delta^{33}\text{S}$ (‰)	MEAN	2SD	Co	Ni	As	Se	Te	Bi	Au	Ag
pyrite	Py1, Py1a+b ($\pm$ Au)	2.1		4.2	-0.03	-0.08	0.53	+	+	+	+	+	+	+	+
pyrite	Py2 (Au)	3.3		3.6	-0.08	-0.17	0.55	+	+	+	+	+	+	+	+

+ + + +, major concentration ($> 1\text{ wt\%}$ or $> 10,000\text{ ppm}$); +, minor ($\leq 1\text{ wt\%}$ or $\leq 10,000\text{ ppm}$); +, trace ($< 0.1\text{ wt\%}$ or $< 1000\text{ ppm}$)

a consistent, positive $\Delta^{33}\text{S}$ signature (Fig. 7), indicating a sulfur reservoir at least partially sourced from sedimentary rocks (Selvaraja et al. 2017; LaFlamme et al. 2018a, b; Sugiono et al. 2021; Caruso et al. 2022). The VVF is hosted by volcanic and intrusive rocks in which volcanogenic hydrothermal processes formed VMS deposits with negative $\Delta^{33}\text{S}$ signature (Jamieson et al. 2006; Sharman et al. 2015). The $\Delta^{33}\text{S}$ signature across the VVF indicates that the sulfur reservoir was homogeneous, consistent with a low variance source at depth (c.f., Pettke et al. 1999; Phillips and Powell 2010; Tomkins 2013; Pitcairn et al. 2015, 2021; Patten et al. 2020).

The restricted range of mean $\delta^{34}\text{S}$ values of $2.1 \pm 4.2\text{‰}$ (2SD) and $3.3 \pm 3.6\text{‰}$ (2SD) recorded in Py1 cores and Py2 rims (Table 3), respectively, in the five orebodies (Fig. 7a) suggests the contribution of a homogeneous, reduced sulfur source. Sulfur derived specifically from sedimentary rocks commonly shows extremely variable $\delta^{34}\text{S}$ signatures that reflect strong local controls, based on variations of $\delta^{34}\text{S}$ values recorded in marine pyrite (e.g., LaFlamme et al. 2018a; Pasquier et al. 2021). Therefore, it is unlikely that the source of sulfur for the VVF is sourced entirely from sedimentary rocks. Rather, a common homogeneous sulfur source is suggested, which is in agreement with the small negative $\Delta^{33}\text{S}$ signature recorded in the VVF.

Fluid $f\text{O}_2$ and $f\text{S}_2$ control on gold precipitation in greenstone belts

Hydrothermal fluids associated with orogenic gold systems are typically reduced, lie within several magnitudes of the fayalite-magnetite-quartz buffer (FMQ to FMQ-4), and display an excess of reduced sulfur, particularly, HS^- , H_2S , and S_3^{2-} complexes, that transport gold ($350 \pm 50\text{ °C}$; Mikucki and Ridley 1993; Loucks and Mavrogenes 1999; Williams-Jones and Heinrich 2005; Evans et al. 2006; Pokrovski et al. 2014, 2015, 2022). A variety of physico-chemical fluid processes may lead to gold decomplexation from reduced auriferous fluids.

In the case of the VVF, there is no evidence for gold precipitation associated with fluid cooling or major pH fluctuations. Narrow, cm-, to m-wide QTC vein alteration halos lack acidic alteration assemblages (Figs. 3 and 4), suggesting a near-neutral pH as is common in orogenic gold systems (Goldfarb et al. 2001, 2005; Goldfarb and Groves 2015). Instead, as reduced auriferous fluids are seismically pumped through the crust (Sibson 1981; Sibson et al. 1988; Sibson and Scott 1998; Cox 2016), gold solubility is driven by either an increase in $f\text{O}_2$ or a decrease in $f\text{S}_2$. An increase in $f\text{O}_2$ of a hydrothermal fluid results in decomplexation of sulfur–gold complexes inducing deposition of Au (Palin and Xu 2000; Williams-Jones and Heinrich 2005; Sugiono et al. 2022). Similarly, a decrease in $f\text{S}_2$ through the removal of

reduced sulfur from a hydrothermal fluid leads to a decrease in gold-sulfide complex activity (Seward 1989; McKibben and Eldridge 1990), which can significantly decrease gold solubility and lead to gold precipitation. Monitoring of changing fluid conditions using the pyrite $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values, in combination with Ni, Co, and As distributions and contents, can provide insights into the mechanisms that lead to gold deposition.

Fluid mixing

Studies have shown that fluid mixing between a reduced deep-seated fluid and a more oxidized magmatic fluid, or hypothesized meteoric fluid and seawater, can lead to destabilization of dissolved gold-sulfide complexes and lead to gold precipitation (Uemoto et al. 2002; Bateman and Hagemann 2004). It is possible to investigate fluid mixing using the $\Delta^{33}\text{S}$ signature, whereby several products between different end-member sulfur reservoirs will produce variable $\delta^{34}\text{S}$ – $\Delta^{33}\text{S}$ signatures (Cameron and Hattori 1987; Neumayr et al. 2008; LaFlamme et al. 2018c), and specifically a depleted $\Delta^{33}\text{S}$ signature compared to the two end-members (Barré et al. 2021). Sulfur reservoirs that have been invoked as end-member sulfur sources associated with Neoproterozoic orogenic gold systems include seawater sulfate ($\delta^{34}\text{S}$ between ca. 0‰ and 7‰ and $\Delta^{33}\text{S}$ between ca. -1.5‰ and 0‰ ; Jamieson et al. 2013) trapped as pore waters in supracrustal rocks (Sharman et al. 2015; Beaudoin and Chiaradia 2016) and magmatic sulfur, which could be either transported in magmatic fluids or leached from volcanic rocks ($\delta^{34}\text{S} = 0\text{‰}$ and $\Delta^{33}\text{S} = 0\text{‰}$; Labidi et al. 2013; Fiorentini et al. 2018).

The QTC veins of the VVF display a consistent non-zero, slightly negative $\Delta^{33}\text{S}$ signature in both Py1 and Py2 in all orebodies ($\Delta^{33}\text{S} = \pm 0.03\text{‰}$ and $\pm 0.08\text{‰}$, respectively; Table 3). Moreover, the variable in situ $\delta^{34}\text{S}$ (between -0.4‰ and 6.3‰) and low variance $\Delta^{33}\text{S}$ data (between -0.20‰ and 0.01‰ ; Fig. 7; Table 2) are in good agreement with high-precision, bulk $\delta^{34}\text{S}$ data (ranging between 0.2‰ and 5.9‰ ; Fig. 7; Table 2) and $\Delta^{33}\text{S}$ data (ranging between -0.07‰ and 0‰). However, fluid mixing as gold decomplexation mechanism of seawater sulfate trapped in crustal rocks and magmatic sulfur cannot explain the low variance, negative $\Delta^{33}\text{S}$ signature recorded in vein-hosted Py2 that contains gold mineralization. Fluid mixing of these two sulfur reservoirs would affect $\Delta^{33}\text{S}$ values ($< -0.10\text{‰}$) and thereby change the $\Delta^{33}\text{S}$ signature during Py2 growth (Figs. 7a and 8). The uncertainty associated with SIMS analyses are too large to be able to see if such a change is present here. Nonetheless, variations in bulk analytical uncertainties are small enough to exclude fluid mixing as a gold decomplexation mechanism. Whereas hydrogen and oxygen isotope compositions recorded in quartz, tourmaline, and carbonate of the VVF indicate fluid mixing

between a deep-seated metamorphic and upper crustal fluids (Beaudoin and Pitre 2005; Beaudoin and Chiaradia 2016), the relatively homogeneous $\delta^{34}\text{S}$ - $\Delta^{33}\text{S}$ signature (Fig. 7a), in turn, could be interpreted to indicate that the S budget was dominated by S transported by the metamorphic fluids without significant input of upper crustal sulfur and that fluid mixing was not the driver for gold decomplexation.

Fluid boiling and immiscibility

Pressure variations that cause fluid boiling and immiscibility can fractionate H_2 and $\text{H}_2\text{S}_{(\text{g})}$ from a hydrothermal fluid, thereby increasing the fluid $f\text{O}_2$ (Drummond and Ohmoto 1985; Richards and Kerrich 1993; Wilkinson and Johnston 1996; Palin and Xu 2000; Weatherley and Henley 2013; Hutchison et al. 2020). In a hydrothermal system at 300 °C, near-neutral pH, and $\Sigma\text{S}=0.05$ mol/kg, this shift in fluid $f\text{O}_2$ can result in the destabilization of Au-sulfide complexes and can lead to a tenfold decrease in gold solubility (Roberts 1987; Seward 1989; McKibben and Eldridge 1990). As the $\text{SO}_4^{2-}/\text{H}_2\text{S}$ ratio increases by removal of reduced H_2 and $\text{H}_2\text{S}_{(\text{g})}$, $\delta^{34}\text{S}$ values will decrease by up to 20‰ (Ohmoto and Rye 1979), which has been observed in several magmatic-hydrothermal and orogenic gold orebodies (Peterson and Mavrogenes 2014; Hutchison et al. 2020; Sugiono et al. 2022). Moreover, a significant decrease in gold solubility through As-controlled redox reactions, which causes gold precipitation, can lead to a distinct depletion in $\delta^{34}\text{S}$ signatures recorded between pyrite cores and rims (shift in $\delta^{34}\text{S}$ up to -15‰ ; e.g., Sugiono et al. 2022). Another indicator for oxidizing conditions during gold precipitation is hematite wallrock alteration associated with Au-hosting pyrite showing a negative $\delta^{34}\text{S}$ signature, as observed in the Kalgoorlie gold camp (Yilgarn Craton, Australia; Godefroy-Rodríguez et al. 2020; McDivitt et al. 2022).

In contrast, in the greenstone-hosted VVF, there is no documented evidence for hematite wallrock alteration associated with a decrease in $\delta^{34}\text{S}$ values (Figs. 7a and 8). Instead, $\delta^{34}\text{S}$ values increase from Py1 to homogeneous Py2. Only the Pascalis Gold Trend pyrite records a decrease with slightly higher $\delta^{34}\text{S}$ values (Fig. 7a) in Py1 cores ($\delta^{34}\text{S}=5.2\text{‰}$) compared to homogeneous Py2 rims ($\delta^{34}\text{S}=3.5\text{‰}$). In general, $\delta^{34}\text{S}$ values increase with increasing distance from the LLCfz (Figs. 1b and 7a). However, this range between orebodies (from -0.4‰ to 6.3‰) might also be the result of local operating processes. For example, orogenic gold systems are known to entrain locally derived sulfur from meta-sedimentary rocks at the site of gold precipitation (Chang et al. 2008). By comparison, meta-volcanic rocks contain low sulfur concentrations (Patten et al. 2020). Nonetheless, local entrainment of pore waters trapped in meta-volcanic rocks can have a major impact on fluid $f\text{O}_2$, which can lead to differing $\delta^{34}\text{S}$ values of precipitated pyrite

and might explain the range of detected $\delta^{34}\text{S}$ values across VVF orebodies (Ohmoto 1972; Ohmoto and Rye 1979; Pasquier et al. 2021).

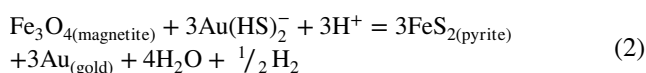
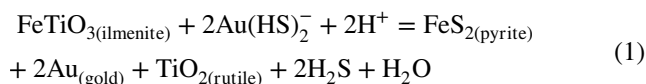
Py1 contains inclusions of carbonate, tourmaline, chalcopyrite, and minor pyrrhotite in combination with elevated Ni and Co concentrations (Tables 2 and 3). Particularly, Ni and Co are both known to derive from increased solubilities at higher $f\text{O}_2$ conditions (Fougerouse et al. 2016; Jansson and Liu 2020). These inclusions in Py1 cores could imply rapid crystallization related to phase separation (Román et al. 2019). However, in the case of phase separation, smaller nm- to μm -sized, inclusions together with low Ni and Co concentrations (Román et al. 2019) are expected as opposed to several tens of μm -large inclusions as well as elevated Ni and Co concentrations recorded in Py1. Moreover, gold inclusions are contained in homogeneous Py2, which lacks textural evidence for phase separation. In the VVF, positive $\delta^{34}\text{S}$ values are in contrast to sanukitoids and intrusion-related gold deposits in the Abitibi subprovince that commonly record a low $\delta^{34}\text{S}$ signature between -25‰ and -5‰ , indicating either a temperature dependent fractionation or high fluid $f\text{O}_2$ conditions associated with gold mineralization (Hastie et al. 2023). Therefore, fluid boiling and immiscibility leading to an increase in fluid $f\text{O}_2$ are not responsible for gold precipitation in the VVF.

Fluid-rock reactions

The Fe-oxide inclusions in Py1 and homogeneous texture in Py2, combined with the increase in $\delta^{34}\text{S}$ values of up to $+3.0\text{‰}$ from early Py1 to Py2 (Figs. 4, 6 and 7), suggest that the removal of reduced, light sulfur, with low $\delta^{34}\text{S}$, from a hydrothermal fluid (i.e., fluid desulfidation; Fig. 9a–b) in a reducing environment led to destabilization of Au-sulfide complexes (Seward 1989; McKibben and Eldridge 1990). Fluid desulfidation-wallrock sulfidation has been proposed to remove sulfur from a hydrothermal fluid that ascends through volcanic rocks (e.g., Goldfarb et al. 2005; Robert et al. 2005; Bi et al. 2011; Ward et al. 2017; Jian et al. 2021; Petrella et al. 2021). The reduced sulfur reacts with Fe-bearing minerals common in greenstone rocks (Phillips 1986; Groves et al. 1998, 2000; Goldfarb et al. 2005; Ward et al. 2017). Such minerals that contain reduced iron (e.g., Fe-rich oxides, carbonates, silicates) either are hosted in igneous wallrock assemblages or occur as a product of wallrock alteration in orogenic gold vein alteration halos. Therefore, Fe-bearing host rock mineral assemblages can significantly enhance fluid desulfidation (i.e., removal of Au-sulfide complexes from a hydrothermal fluid) and, in turn, facilitate wallrock sulfidation (i.e., deposition of sulfides and gold).

The wallrocks of orogenic gold systems in the VVF comprise various intrusive bodies (Fig. 1b), which have all been metamorphosed to regional greenschist facies. These

wallrocks typically contain an igneous assemblage composed to varying proportions of plagioclase, quartz, alkali feldspar, biotite, hornblende and Fe-bearing minerals, particularly ilmenite, titanomagnetite, and magnetite (Fig. 4e–f; Robert and Brown 1986a, b; Groves et al. 1998, 2000; Goldfarb et al. 2005; Rezeau et al. 2017; Dubé 2018; Daver et al. 2020). During fluid-rock reactions leading to wallrock sulfidation (Eqs. 1 and 2), native gold can be precipitated during pyrite growth (Fig. 10a; Reich et al. 2005; Pokrovski et al. 2019).



This, together with an isotopic shift to higher $\delta^{34}\text{S}$ values, suggests that fluid desulfidation not only decreases $f\text{S}_2$ through the removal of sulfur but also induces a small decrease in fluid $f\text{O}_2$ during Py2 growth (Fig. 9a). Based on an isotopic shift to lower $\delta^{34}\text{S}$ values from early pyrrhotite to late arsenopyrite, Petrella et al. (2021) showed that in orogenic gold systems formed by wallrock sulfidation in As-rich meta-sedimentary rocks, an increase in fluid $f\text{O}_2$ would be expected. However, the systematic isotopic shift to higher $\delta^{34}\text{S}$ values between Py1 and Py2 of the VVF, together with native gold and polymetallic Au-Ag-Bi-Te inclusions that are unrelated to zoned areas in Py2 (Fig. 6) with minor and trace concentrations of Ni, Co, or As (Tables 2 and 3), supports a decrease in fluid $f\text{O}_2$ for orogenic gold systems formed in As-poor meta-volcanic rocks by sulfidation of Fe-rich oxides (c.f., Palin and Xu 2000). Daver et al. (2020) document barite and hematite in the VVF that are associated with texturally early pyrite, which support a phase of early pyrite formation under oxidized conditions followed by pyrite growth in more reducing conditions. This implies that pervasive, local fluid-rock interactions, particularly the replacement of Fe-bearing oxides in wallrocks and slivers of wallrocks within veins (Fig. 4b–f; Eqs. 1 and 2), is a main driver to precipitate Py1 and Py2. Subsequent gold precipitation in pyrite is a result of a decrease in gold solubility most likely triggered by intrinsic temperature–pressure fluctuations during wallrock sulfidation in a reducing environment (Fig. 9b; Ohmoto and Rye 1979; Phillips 1986; Palin and Xu 2000; Evans et al. 2006; Ward et al. 2017; Ord and Hobbs 2018; Román et al. 2019).

Wallrock sulfidation drives Au-Ag-Te-Bi inclusion formation

Whereas decreases in fluid $f\text{O}_2$ and $f\text{S}_2$ explain the precipitation of native gold in Py1 and Py2, they fail to account

for the formation of polymetallic Au-Ag-Te-Bi inclusions in Py2 (Figs. 4d, 5a, and 6). Such inclusions are common in the VVF (e.g., Robert 1983; Robert and Brown 1984, 1986a, b; Rezeau et al. 2017; Daver et al. 2020) and have been recognized in similar As-poor orogenic gold systems hosted in meta-volcanic and intrusive rocks, such as in the Mt Pleasant district of the Yilgarn Craton or in the Xiaoqinling district of the North China Craton (Bi et al. 2011; LaFlamme et al. 2018b; Jian et al. 2021). These polymetallic inclusions can form from a gold-undersaturated hydrothermal fluid through the involvement of a co-existing Bi-melt phase, also referred to as low-melting-point-chalcophile element melt (LMCE). Based on thermodynamic models, gold transported as $\text{AuOH}_{(\text{aq})}$ can be deposited on mineral surfaces by Te-Bi-adsorption-reduction mechanisms (Tooth et al. 2008, 2011; Jian et al. 2021). This process has also been proposed for the Neoproterozoic Swayze greenstone belt of the Abitibi subprovince (Hastie et al. 2016, 2020). The Bi-melt gold collector model provides a feasible explanation for the deposition of Au-Ag-Te-Bi inclusions in orogenic gold systems. However, polymetallic inclusions in the orebodies of the VVF differ significantly in Bi-Te composition, compared to inclusions usually associated with an LMCE phase. The latter commonly consist of higher Bi:Te proportions, reflected in the abundance of Bi and maldonite (Au_2Bi) blebs. These globular Bi- and Au-rich blebs have been interpreted to form as a result of oxidized fluid buffering at the pyrrhotite-magnetite boundary and to indicate formation from an LMCE phase (Tooth et al. 2008, 2011). The polymetallic inclusions hosted in Py2 rims are not associated with Bi blebs or Au-rich maldonite inclusions (Fig. 5a–b). Moreover, the formation of a co-existing Te-rich melt phase in a hydrothermal fluid would require the oxidation of Te^- or Te^{2-} species to Te^+ (McPhail 1995). However, the auriferous hydrothermal fluids remained in a reduced state throughout the gold precipitation process, as recorded by the isotopic shift to higher $\delta^{34}\text{S}$ values from Py1 to Py2.

Fluid desulfidation under reducing conditions would be consistent with aqueous transport of reduced Te-species (Zhang and Spry 1994; Keith et al. 2018). Based on telluride mineral stability, the abundance of calaverite (AuTe_2) over petzite (Ag_3AuTe_2) and hessite (Ag_2Te), also recorded by Rezeau et al. (2017) and Daver et al. (2020), in combination with higher $\delta^{34}\text{S}$ values of Py2 suggests that telluride-gold formation likely depended on a coupled decrease of $f\text{Te}_2$ and $f\text{S}_2$ of the hydrothermal fluid (Figs. 10b and 11a–b). Under neutral to alkaline pH, low salinity, high temperature (350 ± 50 °C), and generally low $f\text{O}_2$ hydrothermal fluids, comparable to those recorded in many Neoproterozoic orogenic gold systems, Te solubility will decrease under increasingly reduced conditions. The decrease in fluid $f\text{O}_2$, associated with a decrease in $f\text{S}_2$, in the pyrite stability field, induces a drop in fluid $f\text{Te}_2$ and results in telluride deposition (Afifi

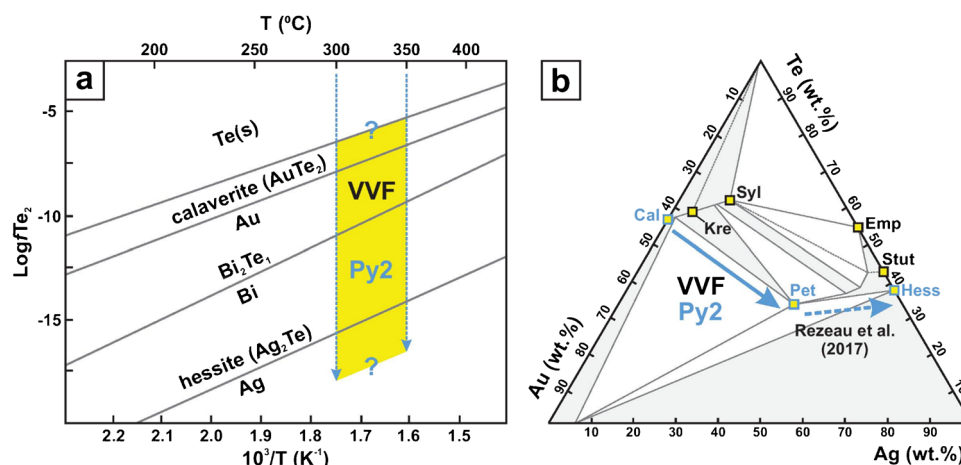


Fig. 11 **a** A $\log f\text{Te}_2$ -temperature diagram showing major telluride mineral formation during Py2 growth, related to decreasing $f\text{Te}_2$ activity in the orogenic gold systems of the VVF. Afifi et al. (1988a, b) Modified from Afifi et al. (1988b). **b** Ternary Au-Ag-Te diagram showing major telluride mineral compositions (< 300 °C) and hydrothermal fluid evolution of the VVF as well as increasingly Ag-rich

tellurides, including hessite, as described by Rezeau et al. (2017) in quartz-tourmaline-carbonate veins of the VVF. Modified after Zhang and Spry (1994), based on data from Markham (1960), Cabri (1965), Legendre et al. (1980), and . Cal=calaverite; Emp=empresite; Hess=hessite; Kre=krennerite; VVF=Val-d'Or Vein Field; Pet=petzite; Stut=stuetzite; Syl=sylvanite

et al. 1988a, b; Zhang and Spry 1994; Cooke and McPhail 2001; Cook et al. 2009; Grundler et al. 2013; Gao et al. 2017; Keith et al. 2018). At approximately 300 °C (Fig. 11a–b), this decrease in $f\text{Te}_2$ leads to precipitation of calaverite and evolved towards increasingly Ag-bearing tellurides, such as petzite (Figs. 10b and 11a–b). Therefore, these phases were incorporated into homogeneous Py2 rims and formed polymetallic Au-Ag-Te-Bi inclusions with different Au:Ag proportions, as a result of coupled decreases in $f\text{O}_2$, $f\text{S}_2$, and $f\text{Te}_2$ of the hydrothermal fluid (Figs. 9, 10, and 11).

Conclusions

Pyrite hosted within QTC vein orebodies (Goldex, Triangle, Plug #4, Pascalis Gold Trend, Beaufor) of the VVF records a minor ubiquitous shift in $\delta^{34}\text{S}$ values of up to +3.0‰ from lighter porous core domains (Py1) to heavier homogeneous rims (Py2) and shows a slightly negative $\Delta^{34}\text{S}$ signature, ranging between –0.20‰ and 0.01‰. Py2 contains most of the associated native gold and polymetallic inclusions (Au-Ag-Te-Bi). The increase in $\delta^{34}\text{S}$ values, combined with, in general, low concentrations in Co and Ni in Py1 cores (< 10,000 ppm), reflects a steady $f\text{O}_2$ and $f\text{S}_2$ decrease. This decrease also led to deposition of Co and Ni in Py1 core domains, as well as the association of texturally-late pyrrhotite with Py2 and the removal of gold-sulfide complexes from the hydrothermal fluid. Our data suggest that a homogeneous fluid reservoir introduced gold-sulfide complexes and that pervasive fluid desulfidation-wallrock sulfidation reactions were

a key mechanism that led to the growth of homogeneous Au-bearing Py2 rims, particularly at the expense of ilmenite, titanomagnetite, and magnetite contained in wallrocks and wallrock slivers within QTC veins. A decrease in the activity of reduced sulfur species drives Au-bearing pyrite precipitation. This reaction is associated with an overall decrease in $f\text{O}_2$ within the pyrite stability field, which, in turn, is responsible for a steady decrease in $f\text{Te}_2$. This decrease initially precipitated calaverite and upon further decrease in $f\text{Te}_2$ evolved towards increasingly Ag-bearing telluride formation, such as petzite, in Py2 rims. Arsenic contents in As-poor porous Py1 cores (all ≤ 67 ppm) and homogeneous Py2 rims (≤ 550 ppm) limit the formation of lattice-bound gold and favor inclusion-hosted gold (Py1, Py1b ≤ 30 ppm, and Py2 ≤ 1250 ppm). The absence of lattice-bound gold, notoriously associated with orogenic gold systems in As-rich rocks, suggests that the VVF presents a prime example for an orogenic gold system that formed in a generally reducing, As-poor (< 0.1 wt%) Archean greenstone belt by fluid-wallrock sulfidation reactions.

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Declarations

Competing interests The authors declare no competing interests.

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