Fluid mixing in orogenic gold deposits: evidence from the H-O-Sr isotope composition of the Val-d'Or vein field (Abitibi, Canada)

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Abstract

Quartz and tourmaline from the Val-d'Or, Québec (Canada) orogenic gold vein field have oxygen isotope fractionation indicating equilibrium over a range of temperature (280-492 °C). The range of $\delta^{18}\text{O}$ values is from 9.2 to 13.8 ‰, and from 6.5 to 9.5 ‰, for quartz and tourmaline, respectively. The hydrogen isotope composition of tourmaline has a range from -63 to -13 ‰. The initial Sr isotope composition ($^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$) of vein tourmaline at the time of mineralization ranged from 0.700710 to 0.702246. Vein carbonates have a similar range in Sr isotope composition, from 0.701243 to 0.703641. A series of samples from the Sigma deposit displays no systematic variation with depth for $\delta^{18}\text{O}$ values of quartz or tourmaline, δD values of tourmaline, temperature of equilibrium, or $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$. The $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ of local komatiite, basalt, andesite, gneiss and granodiorite, at 2.7 Ga, ranged from 0.681971 to 0.7128706. Country rocks with low $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ are likely a consequence of hydrothermal resetting of the Rb/Sr system in these samples.

Covariation of the calculated equilibrium $\delta\text{D}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ with quartz-tourmaline equilibrium temperatures indicates mixing between a low- $\delta^{18}\text{O}$ (< 1.5 ‰), high δD (> -10 ‰), low temperature (< 280 °C) upper crustal fluid, and a high- $\delta^{18}\text{O}$ (> 9.3 ‰), low δD (< -40 ‰), high temperature (> 490 °C) deep-seated metamorphic fluid. At temperatures below the critical point for low-salinity hydrothermal fluids, $\delta\text{D}_{\text{H}_2\text{O}}$ are affected by liquid-vapour phase separation, yielding the high δD values characteristic of the upper crustal fluid. A broad covariation between $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and the $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ of tourmaline is consistent with mixing of two fluids from two reservoirs with different Sr concentrations and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values. The low $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (< 0.7007) inferred for the deep-

seated metamorphic fluid end-member is consistent with Archean prograde metamorphic dewatering of typical volcanic and sedimentary country rocks of the Val-d'Or area. The higher $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (>0.7022) of the upper crustal fluid end-member most likely resulted from a long history of water-rock exchange between Archean seawater and carbonate and radiogenic plutonic rocks of the Abitibi sub-province.

Keywords: stable isotope, radiogenic isotope, oxygen, hydrogen, strontium, gold, vein, hydrothermal fluid

1. Introduction

Orogenic gold deposits consist of auriferous quartz veins with carbonate, sulphide, and a range of accessory minerals including tourmaline (Goldfarb et al., 2005). The quartz in many deposits forms ribboned lenses in steeply dipping reverse shear zones, or flat to shallow-dipping extensional veins. The auriferous quartz vein fields are interpreted to have formed near the base of the seismogenic crust and in the vicinity of major crustal faults (Boullier and Robert, 1992; Groves et al., 1998; Sibson et al., 1988). These fractured domains of the seismogenic crust are interpreted to represent openings during fluid pressure build-up before, and during aftershock slip following major earthquakes (Boullier and Robert, 1992). These gold deposits are hosted in metamorphic belts that formed in transpressional orogens (Goldfarb et al., 2005; Groves et al., 1998; Groves et al., 2003; Kerrich and Wyman, 1990). This geological setting allows studying the infiltration of deep-seated hydrothermal fluids and their interaction with the country rocks in a fossilized hydrothermal system.

The Val-d'Or orogenic gold vein field, Abitibi, Canada (Robert, 1994), is a classical example of this type of deposit with a well-constrained geological setting. The Val-d'Or vein field contains a large number of quartz-tourmaline-carbonate veins with a homogeneous mineralogy, formed in the same structural setting, and interpreted to have formed in a single hydrothermal system (Robert, 1994). The stable isotope compositions (C, O, S) of orogenic gold quartz veins of the Val-d'Or vein field have been documented in detail at the deposit and vein field scales (Beaudoin and Pitre, 2005), who showed that the stable isotope systematics were the result of fluid-rock reaction and mixing between an upper crustal fluid and a deep-seated metamorphic hydrothermal fluid. The regional pattern of vein quartz oxygen isotope composition was reproduced using 3D numerical models simulating transport, reaction and mixing, to demonstrate that the major crustal shear zone controlling the distribution and structural evolution of the auriferous orogenic veins functioned as an episodic hydraulic drain during seismic events (Beaudoin et al., 2006).

This paper presents oxygen isotope composition from coexisting quartz and tourmaline, hydrogen isotope composition from tourmaline, and Rb, Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ data from vein tourmaline and carbonate, as well as representative volcanic, plutonic and sedimentary country rocks. It provides, to date, the most detailed documentation of the combined H-O-Sr isotope systems in vein minerals at the scale of an orogenic gold vein field. The combination of stable and radiogenic isotope systems is used to assess isotope equilibrium as well as hydrothermal fluid compositions and sources that formed the gold veins of the Val-d'Or vein field. The auriferous fluid compositions and sources in the Val-d'Or vein field are compared to those for other orogenic gold districts to show

that fluid mixing is a more common process than commonly recognized in orogenic gold deposits.

2. Geological setting

The Val-d'Or orogenic gold vein field is located at the boundary between the Abitibi volcanic and the Pontiac sedimentary sub-provinces of the Archean Superior Province in Canada (Card and Ciesielski, 1986). The Cadillac-Larder Lake Tectonic Zone (CLLTZ), a major reverse shear zone more than 200 km long and with a steep dip to the north (Robert et al., 1995), separates the Abitibi and Pontiac sub-provinces (Fig. 1). The volcanic rocks of the Abitibi sub-province host most of the quartz-tourmaline-carbonate veins, although some veins also occur within the metasedimentary rocks of the Pontiac sub-province immediately south of the CLLTZ (Figure 1). The volcanic rocks consist of tholeiitic ultramafic to calc-alkaline felsic rocks that erupted between 2714 Ma and 2702 Ma (Pilote et al., 1998; Scott et al., 2002). Desrochers and Hubert (1996) proposed that ultramafic and mafic rocks formed several terranes that were accreted to form the Malartic Composite Block during a first phase of deformation (D_1). They interpreted the calc-alkaline felsic volcanic and volcanoclastic rocks of the Val-d'Or Formation to be deposited above an angular discordance. Scott et al. (2002), however consider that the Val-d'Or Formation is in gradational contact with the underlying mafic rocks. The volcanic pile was intruded by the synvolcanic Bourlamaque Batholith at 2700 Ma (Wong et al. 1991). A second phase of deformation (D_2) was responsible for the dominant E-W foliation that formed during an oblique collision event (Robert 1989; Desrochers and Hubert 1996) that ended with a dextral transcurrent deformation event (D_3) along the CLLTZ (Robert et al. 1995; Neumayr et al. 2000). D_2 shortening was

accommodated by a series of dominantly E-W subvertical to moderately-dipping reverse shear zones that contain the orogenic gold quartz-tourmaline carbonate veins. Prograde greenschist metamorphism associated with D₂ peaked before 2693 Ma (Hanes et al. 1992) to 2677 Ma (Feng et al., 1992). Syn- to late-tectonic plutons have ages ranging from 2694 Ma to 2680 Ma (Wong et al., 1991; Jemielita et al., 1990; Zweng et al., 1993; Couture et al., 1994; Morasse et al., 1995).

2.1 Orogenic gold quartz veins

Cross-cutting relationships between shear zone-hosted gold quartz veins and 2690-2685 Ma syntectonic intrusions indicate two events of gold mineralization (Robert 1994; Couture et al., 1994; Pilote et al., 1998). Early quartz-carbonate auriferous veins are commonly folded and boudinaged within sub-vertical shear zones and cut by dykes (Couture et al., 1994; Robert 1994). The more abundant, younger auriferous quartz - tourmaline-carbonate veins crosscut all intrusive rocks of the region (Robert et al., 1995). The veins form either fault-filled quartz lenses in sub-vertical reverse shear zones, or sub-horizontal extensional veins near the shear zones (Robert et al., 1995).

The samples come from both sub-vertical and from sub-horizontal veins where quartz and tourmaline are intergrown. The proportion of quartz and tourmaline in the vein samples varies from less than 5% to more than 50% tourmaline. Beaudoin and Pitre (2005) showed that there is no systematic variation in oxygen isotope composition from various textural types of quartz in vein, between sub-horizontal extensional and sub-vertical shear veins, and along strike or down-dip within a vein system. A systematic change in $\delta^{18}\text{O}$ values, however, was shown for different deposits. The samples

selected for this study are representative of the range in $\delta^{18}\text{O}$ values and spatial distribution within the Val-d'Or vein field (Beaudoin and Pitre, 2005; Olivo et al., 2006).

3. Analytical methods

Quartz, tourmaline and carbonate concentrates were handpicked under a binocular microscope. Sub-samples of quartz and tourmaline, weighing 7-10 mg, were reacted with BrF_5 according to the method of Clayton and Mayeda (1963) at the Stable Isotope Laboratory of Université Laval. The evolved CO_2 was analyzed by IRMS at the G.G. Hatch Laboratory of the University of Ottawa. Oxygen isotope ratios are reported in the δ -notation relative to V-SMOW with a precision better than 0.2 ‰ (1σ). Accuracy and precision of $\delta^{18}\text{O}$ values was verified by analysis of NBS-28. Tourmaline hydrogen isotope composition was measured using a Carlo Erba Elemental Analyzer NCS2500 coupled to a Finnigan MAT 252 Isotope Ratio Mass Spectrometer at Queen's Isotope Facility. Hydrogen isotope ratios are reported in the δ -notation relative to V-SMOW with a precision better than 2 ‰ (1σ).

Whole-rock major and trace elements were measured for eight volcanic, six plutonic, and three sedimentary rocks, using Li-borate fusion inductively coupled plasma (ICP) and inductively coupled plasma mass spectrometry (ICP-MS) analysis at Actlabs (Ancaster, Canada). The Sr and Rb contents, and Sr isotope composition of tourmaline were measured on 17-54 mg sub-sample aliquots. Tourmaline concentrates were reacted with 2.2 N acetic acid to dissolve residual carbonate, rinsed three times in deionized water (18 Mohm/cm), dissolved in a 1:4 mixture of 15M HNO_3 and 29M HF at 160°C in sealed Teflon vials, and finally evaporated to dryness. The dried residue was dissolved in 1.9 mL of 1M HNO_3 , and the Rb and Sr contents were measured on an

aliquot of 0.950 mL by ICP-MS at Actlabs (Ancaster, Canada). Detection limits for Rb and Sr were 10 and 20 ppb, respectively. The Sr for isotopic analysis was purified from the remaining solution aliquot (0.950 mL) using a Sr-spec resin column. The purified Sr was loaded on single Re filaments with a Ta oxide solution. Sr isotope ratios were measured at the Department of Earth Sciences (Geneva, Switzerland) in a Thermo Triton thermal ionization mass spectrometer using Faraday cups at a pyrometer-controlled temperature of 1480°C in static mode, and using the virtual amplifier design to cancel out biases in gain calibration among amplifiers. $^{87}\text{Sr}/^{86}\text{Sr}$ values were internally corrected for fractionation using a $^{88}\text{Sr}/^{86}\text{Sr}$ value of 8.375209. Raw values were further corrected for external fractionation by a value of +0.03‰, determined by repeated measurements of the SRM987 standard ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710248$; McArthur et al., 2001). External reproducibility of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the SRM987 standard is 14 ppm (2 σ).

For carbonate minerals, a few mg of sample was dissolved in 2.2 M high purity acetic acid during 1 to 2 hours at room temperature. The solution was centrifuged and the supernatant was evaporated. The residue was dissolved in a few drops of 14 M HNO_3 and Sr was separated from the matrix using a Sr-Spec resin. The purified Sr was dissolved in 5 ml of ~2% HNO_3 solution. Sr isotope ratios were measured using a Thermo Neptune PLUS Multi-Collector ICP-MS in static mode. The $^{88}\text{Sr}/^{86}\text{Sr}$ (8.375209) was used to monitor internal fractionation. Interferences at masses 84 (^{84}Kr), 86 (^{86}Kr) and 87 (^{87}Rb) were corrected by monitoring ^{83}Kr and ^{85}Rb . The SRM987 standard was used to check external reproducibility, which on the long-term (90 measurements from April to September 2014) was 17 ppm (2 sigma: 0.710276 ± 0.000012). The $^{87}\text{Sr}/^{86}\text{Sr}$ values were corrected for external fractionation, based on a systematic difference

between the measured and the nominal $^{87}\text{Sr}/^{86}\text{Sr}$ value of SRM987 of 0.710248 (McArthur et al., 2001), by a value of -0.039‰ per amu.

4. Results

4.1 Oxygen and hydrogen isotope composition of orogenic gold vein tourmaline and quartz

The oxygen isotope composition of quartz shows a range from 9.2 to 12.5 ‰, similar to those reported from quartz-tourmaline-carbonate veins in the Val-d'Or vein field (Table 1; Fig. 1; 9.2-13.8 ‰; Beaudoin and Pitre, 2005; Olivo et al., 2006). The range of tourmaline $\delta^{18}\text{O}$ values is from 6.5 to 9.5 ‰ with one higher value at 11.4 ‰, in sample 96-DP-15, which, in contrast to the other samples, contains quartz detected by X-ray diffraction (Table 1). A $\delta^{18}\text{O}$ - $\delta^{18}\text{O}$ plot of quartz versus tourmaline shows a linear array with a slope near unity, with the exception of sample 96-DP-15, indicating that the quartz-tourmaline pairs appear to be in oxygen isotope equilibrium (Fig. 2A).

Three quartz-tourmaline oxygen isotope fractionation equations have been proposed in literature, which yield slightly different temperatures of equilibrium (Blamart, 1991; Kotzer et al., 1993; Zheng, 1993). Equilibrium temperatures computed using Blamart (1991) range from 414 to 566°C, whereas Zheng (1993) fractionation yields a slightly lower average temperature of 418 °C but a larger range of values from 308 to 568°C. Kotzer et al. (1993) fractionation yields a lower average temperature of 366 °C from a range of 280 to 492 °C (Table 1). The equilibrium temperatures computed using Kotzer et al. (1993) empirical fractionation are considered more representative of the hydrothermal system temperature based on other geothermometers and fluid inclusion trapping temperatures (Beaudoin and Pitre, 2005). Using the quartz-tourmaline

temperature of oxygen isotope equilibrium from Kotzer et al. (1993), the $\delta^{18}\text{O}$ value of quartz, and the quartz- H_2O fractionation of Matsuhisa et al. (1979), the $\delta^{18}\text{O}$ of water in equilibrium with quartz is estimated to have varied from 2.8 to 9.3 ‰ (Table 1).

The $\delta^{18}\text{O}$ values of coexisting quartz and tourmaline are plotted in Figure 2B against the oxygen isotope fractionation between coexisting quartz and tourmaline ($\Delta_{\text{Qz-Tur}}$). Figure 2B shows that smaller $\Delta_{\text{Qz-Tur}}$ values are associated with higher tourmaline $\delta^{18}\text{O}$ values, and that larger $\Delta_{\text{Qz-Tur}}$ values characterise tourmaline with lower $\delta^{18}\text{O}$ values. The range in $\Delta_{\text{Qz-Tur}}$ values (1.8 ‰) is 3 times larger than the uncertainty of ± 0.3 ‰ (Fig. 2B). Figure 2C is a plot of $\Delta_{\text{Qz-Tur}}$ values or the temperature of quartz-tourmaline oxygen isotope equilibrium, using Kotzer et al. (1993), versus the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ computed from $\delta^{18}\text{O}_{\text{Qz}}$ and the fractionation of Matsuhisa et al. (1979), and from the $\delta^{18}\text{O}_{\text{Tur}}$ and the fractionation of Kotzer et al. (1993). Because of the difference in the calibration of the fractionations, the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ computed from tourmaline are systematically lower by about 1.5‰ compared to quartz (Fig. 2C). The equilibrium temperature shows a covariation between a low-temperature, low- $\delta^{18}\text{O}$ end-member, and a high-temperature, high- $\delta^{18}\text{O}$ end-member (Fig. 2C). The T- $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ relation reflects the fact that the smaller $\Delta_{\text{Qz-Tur}}$ values, or higher temperatures, are associated with higher $\delta^{18}\text{O}_{\text{Tur}}$ values (Fig. 2B), or a heavier fluid in terms of oxygen isotope composition. Conversely, larger $\Delta_{\text{Qz-Tur}}$ values (or lower T) are associated with lower $\delta^{18}\text{O}_{\text{Tur}}$ values (Fig. 2B), or a lighter fluid in terms of oxygen isotope composition.

Thirteen samples were collected from the Sigma deposit at depths below surface ranging from 389 m (1128Stope#1) to 1338 m (32L-XCut19, Table 1, Fig. 3). Neither the oxygen isotope compositions of quartz (n=13) and tourmaline (n=6), nor the temperature

of isotope equilibrium display a systematic variation with depth (Fig. 3). Two samples from upper levels (1128) have the lowest quartz and tourmaline $\delta^{18}\text{O}$ values and lower oxygen isotope equilibrium temperatures. However, there is no systematic variation in oxygen isotope composition and equilibrium temperature with depth (Fig. 3). A high temperature of equilibrium (491 °C) is computed for sample 23LXcut#12 at ~900 m depth, but the apparent trend is reversed for the deepest sample (32LXcut#19), which shows lower $\delta^{18}\text{O}_{\text{tur}}$ values and lower equilibrium temperature (Fig. 3).

Tourmaline δD values have a range from -69 to -13‰ (Table 1). Using Kotzer et al. (1993) for hydrogen isotope tourmaline-water fractionation and the quartz-tourmaline oxygen isotope equilibrium temperature, the $\delta\text{D}_{\text{H}_2\text{O}}$ values in equilibrium with tourmaline have a range from -34 to 29‰ (Table 1). The tourmaline δD and $\delta^{18}\text{O}$ values plot as a steeply dipping array in Figure 4A. The composition of water in equilibrium with tourmaline and quartz also forms an array with two end-members, one with a lower δD of -34‰ and a higher $\delta^{18}\text{O}$ of 7.6‰, and the second with a higher δD of 29‰ and a lower $\delta^{18}\text{O}$ of 1.5‰ (Fig. 4A). Figure 4B shows a plot of water hydrogen isotope composition in equilibrium with tourmaline versus the quartz-tourmaline oxygen isotope temperature of equilibrium. Samples with temperatures of equilibrium between 400 and 500°C plot along a linear array characterized by low $\delta\text{D}_{\text{H}_2\text{O}}$ (-34 ‰) at high temperature, and higher $\delta\text{D}_{\text{H}_2\text{O}}$ (19 ‰) at 400 °C (Fig. 4B). At temperatures lower than 400°C, the linear relation is broken and the δD values of water show no relation to temperature (Fig. 4B).

4.2 Rb-Sr and Sr isotope composition of orogenic gold vein tourmaline and carbonate

The tourmaline Sr concentrations vary from 49 to 935 ppm, whereas Rb concentrations range from 0.01 to 9.52 ppm (Table 1). Rb/Sr ratios are low, from 0.047×10^{-3} to 5.437×10^{-3} , with one value at 32.715×10^{-3} . The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are from 0.701241 to 0.704409 (Table 1). The initial Sr isotope compositions ($^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$), calculated at 2.7 Ga, range from 0.700710 to 0.702246 (Table 1, Fig. 5). The age of the quartz-tourmaline-carbonate gold veins in the Val-d'Or vein field remains unresolved, hydrothermal mineral ages display a wide range of 107 Ma, from 2.697 to 2.590 Ga, based on a variety of geochronometers (Olivo et al., 2007). The uncertainty in age for the quartz-tourmaline-carbonate gold veins, however, is too small to create significant differences in the $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ reported in Table 1. At the Sigma deposit, the six samples show no systematic variation in $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ with depth (Fig. 3). The variation in $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ correlates neither with 1/Sr (the highest 1/Sr has near average $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$; Fig. 6A), nor with Rb/Sr (Fig. 6B). The sample with the highest Rb/Sr has the lowest $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (Fig. 6B). Moreover, the oxygen isotope equilibrium temperatures, whether above or below the 350°C (Fig. 2A) show no relation with 1/Sr, Rb/Sr or $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (Figs. 6A and 6B). The Sr isotope composition of 2 vein carbonates (0.701700 and 0.703514) from early QC veins is similar to that of 5 vein carbonates from later QTC veins that have $^{87}\text{Sr}/^{86}\text{Sr}$ ranging from 0.701243 to 0.703641, excluding one value at 0.709624. The $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ of vein tourmaline and carbonate are similar, including the high carbonate value that is not unlike other tourmaline in the Abitibi sub-province (Table 1, Fig. 5).

4.3 Rb-Sr and Sr isotope compositions of regional country rocks

Representative samples of regional country rocks were selected to document the contents of Rb, Sr, and the Sr isotope compositions of the host rocks in the Val-d'Or area. The samples are from andesitic to komatiitic volcanic rocks, syn-volcanic intrusive granodiorite of the Bourlamaque Batholith and Bevcon pluton, post-volcanic intrusive rocks of the Sullivan Pluton, and grauwackes (Table 2). Andesite and basalt contain between 60 and 295 ppm Sr, and between 6 and 11 ppm Rb, excluding one sample with 109 pm Rb (Table 2). Komatiitic rocks have up to 27 ppm Sr, and less than 3 pm Rb (Table 2). Intrusive rocks have similar Sr and Rb contents, respectively, from 122 to 227 ppm, and from 16 to 44 ppm. Grauwackes have between 175 and 817 ppm Sr and Rb, and between 21 and 82 ppm Rb (Table 2). The measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.704961 to 0.891088 (Table 2). The initial Sr isotope compositions ($^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$), calculated at 2.7 Ga, range from 0.681971 to 0.7128706 (Table 2, Fig. 5). Volcanism in the Val-d'Or area occurred from 2714 to 2702 Ma (Scott et al., 2002), but the small differences between the ages of volcanic rocks at 2.7 Ga results in insignificant differences in their estimated $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$. The difference between intrusion age and the model age of 2.7 Ga also induces insignificant differences in $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$. The $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ displays no correlation with 1/Sr (Fig. 6C) or Rb/Sr (Fig. 5D). The basalt sample (96-DP-95) with the highest Rb/Sr (1.81) has a low Sr content (60 ppm) and the lowest $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$, (0.681971, Fig. 6D). Three samples have $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ below the Basaltic Achondrite Best Initial (BABI) of 0.69897 (Faure, 1986). Two of these samples, with $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ below the BABI value, plot away from the model 2.7 Ga isochron.

5. Discussion

5.1 Sources of hydrothermal fluids

Quartz and tourmaline from the Val-d'Or orogenic gold vein field display evidence for oxygen isotope equilibrium over a range of temperatures (280-492 °C, average of 366 ± 74 °C) and ranges of $\delta^{18}\text{O}$ values for quartz (3.3 ‰) and tourmaline (3 ‰; Fig. 2A). The range in oxygen isotope equilibrium temperatures compares well with other isotope geothermometers and estimated fluid inclusion trapping temperatures (Beaudoin and Pitre, 2005). The variation in quartz and tourmaline oxygen isotope compositions and equilibrium temperatures is similar to that reported for the Val-d'Or vein field by Beaudoin and Pitre (2005) and Olivo et al. (2006). The oxygen isotope composition for quartz and tourmaline have been interpreted to indicate that the hydrothermal fluids had a range of oxygen isotope compositions as a result of water-rock exchange and mixing between two end-member components (Beaudoin and Pitre, 2005).

Beaudoin and Pitre (2005) showed that the quartz $\delta^{18}\text{O}$ values have a variance, at the deposit-scale, which is similar to the analytical precision (± 0.2 ‰). Quartz $\delta^{18}\text{O}$ values (this study) from the Sigma deposit have a spread (2.9 ‰) slightly less than the range in compositions (4.6 ‰) for the whole vein field (Beaudoin and Pitre, 2005). The average composition of quartz at Sigma (11.2 ‰) is similar to that (11.1 ‰) found by Olivo et al. (2006), but the standard deviation of our results (± 0.9 ‰) is larger compared to that (0.1 ‰) obtained by Olivo et al. (2006). Combining the results of this study with those of Beaudoin and Pitre (2005) and Olivo et al. (2006), the average $\delta^{18}\text{O}$ value for the Sigma deposit is 11.2 ± 0.7 ‰ ($n = 26$). The larger variability of our results at Sigma compared to previous studies in the Val-d'Or vein field, which showed no systematic oxygen isotope variance with quartz texture or structural style (Beaudoin and Pitre, 2005; Olivo et al., 2006), remains unexplained, as Figure 3 shows no systematic

variation with depth for either $\delta^{18}\text{O}_{\text{Qz,Tur}}$ or the temperature of oxygen isotope equilibrium, whereas quartz and tourmaline pairs are in oxygen isotope equilibrium.

The oxygen isotope composition of water in equilibrium with quartz and tourmaline is estimated, for the whole vein field, to vary from 2.9 to 9.3 ‰, using quartz $\delta^{18}\text{O}$ values, or from 1.5 to 7.6 ‰ using tourmaline $\delta^{18}\text{O}$ values, and the quartz-tourmaline equilibrium temperature (Table 1). The difference in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values computed using quartz and tourmaline is likely a consequence of a small discrepancy in the absolute calibration of the fractionations between the two minerals and water. This range is similar but slightly larger than that of hydrothermal fluid compositions (3.9-8.5 ‰) calculated by Beaudoin and Pitre (2005) from quartz $\delta^{18}\text{O}$ values and using the assumption of isothermal conditions at 350 °C.

The covariation of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ with quartz-tourmaline fractionation or oxygen isotope equilibrium temperatures (Fig. 2C) results from the larger difference in quartz and tourmaline oxygen isotope compositions for tourmalines with lower $\delta^{18}\text{O}$ (Fig. 2B). Quartz and tourmaline yield similar values for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ at a given temperature, the difference representing small errors in the calibration of the mineral water fractionations. This covariation indicates that quartz and tourmaline oxygen isotope compositions record mixing between two hydrothermal fluids at the scale of the vein field. The low- $\delta^{18}\text{O}$ (< 1.5 ‰) fluid end-member had a lower temperature (<280 °C) than the high- $\delta^{18}\text{O}$ (>9.3 ‰), hydrothermal fluid end-member ($T > 492$ °C; Fig. 2C).

The hydrogen isotope composition of water in equilibrium with tourmaline (-34 to 29‰, Table 1) partially overlaps with values from previous studies on tourmaline from orogenic gold deposits in the Trans-Hudson Orogen, Canada (Ansdell and Kyser, 1992; Fedorowich et al., 1991; He, 1998; Hrdy and Kyser, 1995; Ibrahim and Kyser, 1991;

Schultz, 1996) and extend the range towards higher δD values (Fig. 4A). Water in oxygen and hydrogen isotope equilibrium with tourmaline from Val-d'Or, and from other orogenic gold deposits, forms a linear array that extends from values typical of metamorphic water to values that plot on the projection of the meteoric water line at δD and $\delta^{18}O$ values higher than that of seawater (Fig. 4A), similar to values computed from sericite and chlorite at the Racetrack deposit, Australia (Hagemann et al., 1994). A pristine meteoric water origin for this fluid component, however, is unlikely for several reasons, as discussed below.

The Val-d'Or orogenic vein field formed at ca. 2.7 Ga, during deformation and metamorphism of a volcanic arc that was becoming emergent. This environment is unlikely to lead to meteoric water with δD and $\delta^{18}O$ values higher than that of seawater. The depth of formation of the veins, near the base of seismogenic crust (Boullier and Robert, 1992), implies that any surficial fluid should have percolated at great depths (ca. 10 km) to reach the domain of vein formation. It is most likely that water-rock reactions would have modified the oxygen and hydrogen isotope composition of meteoric water during its advection into the crust as shown by numerous studies since Taylor (1971). In addition, the water hydrogen isotope composition is heavier than that of seawater, such that water-rock reactions cannot produce water with δD values higher than that of the rocks or water. Late hydrogen isotope exchange between tourmaline and meteoric water cannot be invoked because it would have caused low δD values.

The composition of tourmaline precipitated from a fluid with a fixed composition ($\delta^{18}O = 5 \text{ ‰}$; $\delta D = 0 \text{ ‰}$), and along a temperature gradient from 500° to 300°C, yields a trajectory of $\delta^{18}O$ and δD values from 7.0 to 9.7 ‰ and from -17 to -55, respectively, not unlike the composition of the Val-d'Or tourmaline. If tourmaline had precipitated from a

fluid with a fixed composition, however, quartz in equilibrium the tourmaline must precipitate under the same conditions, and this would yield an array of quartz-tourmaline $\delta^{18}\text{O}$ values perpendicular to the isotherm model lines in Figure 2A. In contrast, the quartz and tourmaline oxygen isotope compositions spread along the isotherm model lines, such that each must have precipitated from a fluid of different oxygen isotope composition, as shown by Gregory et al. (1989).

The hydrogen isotope composition of the fluid could become gradually enriched in D by precipitation of isotopically light hydrous silicates, such as tourmaline, chlorite, muscovite or biotite. A computation of the composition of tourmaline formed by an open system Rayleigh process shows that the range in $\delta^{18}\text{O}$ and δD values of Val-d'Or tourmaline can only be reproduced at very small residual fractions of the fluid (0.1). The boron content of the hydrothermal fluids at the Sigma deposit has been estimated to have ranged between 7×10^{-3} and 0.21 m B (Garofalo, 2000), such that the amount of tourmaline that can precipitate from this concentration cannot deplete the hydrothermal fluid of more than 99% of its oxygen and hydrogen. An increase in δD values, however, could perhaps be caused by local precipitation of massive tourmaline in veins.

The covariation of $\delta\text{D}_{\text{H}_2\text{O}}$ values with temperature between 500 and 400 °C (Fig. 4B) suggests that tourmaline precipitated from fluids of varying temperature and composition. The most likely hypothesis to explain temperature-composition variations in a fluid is mixing, consistent with the oxygen isotope data (Fig. 2C). The array of $\delta\text{D}_{\text{H}_2\text{O}}$ values is interpreted to record mixing between a high temperature (> 492 °C), low δD ($< -40\text{‰}$) fluid of metamorphic origin, as shown in Figure 4A, and a lower temperature fluid with a range of higher δD values, as discussed below.

At temperatures lower than 400°C, the linear relation between δD_{H_2O} and temperature is broken and δD_{H_2O} values become more variable (Fig. 4B). This occurs at temperatures below the critical point of the low salinity (3-7 wt. % NaCl eq.) fluids typical of orogenic gold deposits (Ridley and Diamond, 2000). This indicates that the second fluid component, with high δD values (Fig. 4A), has a more complex origin. Figure 4B suggests that at temperatures lower than 400 °C, at least two sub-components exist, one with δD near -10‰, and the other with δD values above 30‰. The first sub-component with δD values near -10‰ is most likely seawater or perhaps meteoric water trapped in bedrock pores where it underwent oxygen isotope exchange. The second sub-component is more speculative. Liquid-vapour phase separation in 1m NaCl solutions typical of orogenic gold deposits yields a maximum hydrogen isotope fractionation of -5 ‰ at 320 °C (Horita et al., 1995). When overpressured fluids activate a fault-valve system (Sibson et al., 1988), the pressure drop will cause phase separation, as shown in the Val-d'Or vein field (Robert et al., 1995). It is likely that this vapour will migrate more rapidly than the residual liquid, and then condense under increasing pressure once the fault-valve becomes sealed again. In the closed system of a pressurized vein, the vapour will condense entirely to liquid retaining the heavy isotopic composition of the initial vapour. Successive episodes of water boiling and vapour migration, typical of the dynamic vein system under fluctuating pressure (Robert et al., 1995), can yield the high δD value fluid component. Most likely, the fraction of vapour will condense within a fracture that may have contained water variably modified by water-rock reactions and previous episodes of liquid-vapour phase separation, to yield the highly variable δD_{H_2O} values below about 400 °C (Fig. 4B).

The fact that δD_{H_2O} values are heterogeneous below the temperature of the critical point of low salinity water solutions suggest that the separation of liquid water and vapour below that temperature is a likely cause for the high, and variable, δD_{H_2O} values. In contrast to hydrogen, the separation of vapour from a low salinity solution will cause a small oxygen isotope fractionation, of less than 1‰, at 350°C (Horita et al., 1995). Liquid-vapour phase separation is also indicated by the boron isotope composition of tourmaline in veins of the Val-d'Or orogenic gold deposits (Beaudoin, 2013).

The arrays of δD_{H_2O} and $\delta^{18}O_{H_2O}$ values versus temperature are best explained by mixing of two main fluid end-member compositions. The low temperature (< 280 °C), low $\delta^{18}O$ (< 1.5 ‰) and high δD (> -10 ‰) hydrothermal fluid end-member is consistent with an upper crustal origin (Figs. 2C and 4A), most likely from Archean seawater trapped in the country rock porosity. Mineral-water and liquid-vapour hydrogen isotope fractionations (at temperatures lower than ~400 °C) best explain the variable, and high, δD_{H_2O} values of the upper crustal fluid end-member. The high temperature (> 490 °C), high- $\delta^{18}O$ (> 9.3 ‰) and low δD (< -40 ‰) of the second hydrothermal fluid end-member (Figs. 2C and 4A) suggest an origin by prograde metamorphic dewatering of the country rocks, as proposed by Beaudoin and Pitre (2005) for the Val-d'Or vein field, and by Olivo et al. (2006) for the Sigma deposit.

5.2 Strontium isotope composition of auriferous hydrothermal fluids

Figures 6A and 6B show that tourmaline from Val-d'Or displays no systematic variation in Sr isotope composition in relation to the Rb and Sr content, whatever the temperature of oxygen isotope equilibrium between coexisting quartz and tourmaline.

Compared to other orogenic gold vein tourmaline and other minerals, Val-d'Or vein tourmaline has similar 1/Sr and Rb/Sr (Fig. 7). In the $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ versus 1/Sr diagram (Fig. 7A), tourmaline dominantly form a narrow array toward 1/Sr~ 0.025, similar to Archean hydrothermal carbonates (Veizer et al., 1989b). In Val-d'Or and elsewhere in the Abitibi sub-province, tourmaline samples with the highest Rb/Sr plot at low $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (Fig. 7B), such that the range in $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ is not a consequence of variation of the Rb content of tourmaline. Instead, the tourmaline $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ corresponds most likely to that of the fluid from which it precipitated as concluded elsewhere in the Abitibi sub-province (King and Kerrich, 1989). This hypothesis is also supported by the oxygen isotope equilibrium between coexisting quartz and tourmaline over a range of temperatures (Fig. 2A). Because the strontium isotope composition of tourmaline is not a function of temperature, the range in tourmaline $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.70071 to 0.70225) must indicate that the auriferous hydrothermal fluids had the same range in strontium isotope composition.

The $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ values of tourmaline display a broad negative covariation with the oxygen isotope composition of hydrothermal fluids (Fig. 8). As shown in Figures 2C and 4B, the oxygen and hydrogen isotope compositions of the hydrothermal fluids covary also with the temperature of isotope equilibrium. In contrast to hydrogen and oxygen, the strontium isotope composition of tourmaline is independent of the temperature of equilibrium, and depends only on the composition of the hydrothermal fluid. The covariation of oxygen and strontium isotope composition of hydrothermal fluids must therefore result from mixing between two fluid end-members with different oxygen and strontium isotope compositions: (i) the upper crustal, high δD , low $\delta^{18}\text{O}$, high temperature fluid end-member was characterized by higher $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$, whereas (ii) the deep-seated, metamorphic, low δD , high $\delta^{18}\text{O}$, high temperature fluid end-member had a

less radiogenic Sr isotope composition (Fig. 8). Lack of covariation between $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ and $1/\text{Sr}$ led King and Kerrich (1989) to conclude that the range in strontium isotope composition of Abitibi tourmalines was not caused by mixing. Strontium and oxygen isotope binary mixing of two fluids with identical Sr concentrations will yield a straight line in a $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\delta^{18}\text{O}$ diagram (Banner and Hanson, 1990), as shown in Figure 8. Large differences in Sr content will yield hyperbolic mixing trajectories, which show that all but one datum can be modeled by [upper crustal:metamorphic fluid Sr concentration] ratios ranging from 10 to 0.05 (Fig. 8). The tourmaline sample plotting below the model mixing lines has the highest Rb/Sr, and the lowest $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$, which suggests the Rb/Sr system was disturbed in this sample, most likely after formation of the orogenic gold deposits. The range of Sr content ratios (200) in model fluids is larger than the range in Sr concentration in tourmaline

The strontium and oxygen isotope systematics therefore indicate that two types of hydrothermal fluids were mixing in different proportions during the formation of the orogenic gold veins (Figs. 2 and 8). The first end-member hydrothermal fluid had a lower temperature (<280 °C), high δD (>30 ‰), low $\delta^{18}\text{O}$ (<1.5 ‰) but radiogenic $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (>0.7023), whereas the second end-member hydrothermal fluid had a higher temperature (>490 °C), low δD (<-40 ‰), high $\delta^{18}\text{O}$ (<9.3 ‰) and non-radiogenic $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (<0.7007).

5.3 Strontium sources

The Sr content and $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ of the Val-d'Or area country rocks indicate that volcanic and plutonic rocks have low Sr (<2 to 295 ppm) and $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.6820 to 0.7009, and one high value of 0.7031), whereas sedimentary rocks have higher Sr (175-

817 ppm) and $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.7004 to 0.7014). The whole rock $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ below the BABI value most likely indicate that the Rb-Sr system has been affected by alteration in these samples, and they are not considered further. The strontium isotope composition of the local country rocks is consistent with the low $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.7010 to 0.7018) calculated for Archean ultramafic to mafic volcanic rocks in the Abitibi sub-province (Hart and Brooks, 1977; Machado et al., 1986). Low $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.7008 to 0.7016) are also reported for syenite and lamprophyre intrusions in the Abitibi sub-province (Hattori et al., 1996). Granodiorite and tonalite intrusions in the Abitibi sub-province have low to higher $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ values (0.7006 to 0.7031) (Davis et al., 2000; Verpaerst et al., 1980). The local and regional volcanic and plutonic rocks therefore have a strontium isotope composition similar to the composition of the low radiogenic $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ metamorphic fluid. This interpretation is in contrast with that of Kerrich et al. (1987) and King and Kerrich (1989). Based on the difference in Sr content and Sr isotope composition between vein tourmaline and the host rock, and the provinciality of vein tourmaline Sr isotope composition from various gold camps, Kerrich et al. (1987) and King and Kerrich (1989) concluded that the Sr in the veins reflected the source rock, instead of addition of local Sr by fluid-rock exchange. The Sr source for the high $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$, upper crustal hydrothermal fluid is less well constrained. Some altered volcanic rocks and granitic intrusions with high whole-rock $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ could represent a potential source for the radiogenic strontium component in the supracrustal hydrothermal fluid. Another potential source for the radiogenic strontium is found in the Archean carbonates, which have high $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.7025 ± 0.0015) in the Superior province (Veizer et al., 1989a).

In the $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ versus $\delta^{18}\text{O}$ diagram (Fig. 8), the range of tourmaline compositions suggests that the two end-member fluid components had different Sr

contents. Samples plotting above the 1:1 constant Sr content imply that the radiogenic fluids had higher Sr such as found in some of the granodiorite and tonalite intrusions, which have up to about 900 ppm Sr (Davis et al., 2000; Verpaerst et al., 1980). The less radiogenic fluids must have had lower Sr content, as would be expected from water/rock reaction with volcanic and plutonic rocks of the Val-d'Or area (<295 ppm Sr, Table 2) and typical volcanic and plutonic rocks of the Abitibi sub-province (Davis et al., 2000; Hart and Brooks, 1977; Machado et al., 1986). In contrast, samples plotting below the 1:1 model line in Figure 8, imply that the less radiogenic fluids had higher Sr such as those from grauwackes (Table 2) and the lamprophyre and syenite intrusions (375-1900 ppm Sr) of the Abitibi sub-province (Hattori et al., 1996). The low Sr content and radiogenic strontium isotopic hydrothermal fluid compositions are likely a result from water/rock exchange in the source with Sr-poor (<200 ppm) Archean carbonates (Veizer et al., 1989a). It is notable that the range of Sr content in potential strontium sources is similar to that measured in tourmaline (49 to 935 ppm Sr).

5.4 Comparison with hydrothermal fluid Sr isotope compositions in other orogenic gold districts

The Sr isotope composition of scheelite and tourmaline from orogenic gold deposits in the Yilgarn Craton of Western Australia (Fig. 7) ranges from 0.7014 to 0.7028 (Mueller et al., 1991). This range in $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ was interpreted to result from reaction between a radiogenic hydrothermal fluid that was evolved from anatectic magmas in deep-seated granitic batholiths, and the less radiogenic Archean regional country rocks (Mueller et al., 1991). This is in contrast with the Val-d'Or orogenic gold vein field where we show that the high-temperature, high $\delta^{18}\text{O}$, low δD , metamorphic

fluid has low $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ and is likely derived from prograde metamorphism of, and/or water/rock exchange (Beaudoin and Pitre, 2005; Beaudoin et al., 2006) with typical volcanic and plutonic rocks of the Abitibi sub-province. Hydrothermal fluids of metamorphic origin characterized by radiogenic Sr have been proposed for the orogenic gold deposits in the Meguma district, Nova Scotia, Canada (Kontak et al., 1996; Kontak and Kerrich, 1997), and for the Alleghany district, California, U.S.A. (Böhlke and Kistler, 1986). In the Meguma and Alleghany districts, and at the Omai deposit (Guyana; Voicu et al., 2000), the range in fluid Sr isotope compositions is interpreted to have resulted from variable degrees of reaction of the hydrothermal fluids with the regional country rocks. In contrast, the limited range of scheelite Sr isotope compositions (0.7146 to 0.7162) was interpreted to indicate a homogeneous fluid composition at the Muruntau deposit, Uzbekistan (Kempe et al., 2001).

5.5 Fluid mixing in orogenic gold deposits

The stable isotope systematics in the Val-d'Or orogenic gold vein field show a large range in $\delta^{18}\text{O}_{\text{fluid}}$ (6.5‰), $\delta\text{D}_{\text{fluid}}$ (65‰), and $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.0154). The range in $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ cannot be caused by variations in temperature or pressure. The range of fluid $\delta^{18}\text{O}$ and δD values is a consequence of the variation of temperatures of equilibrium (~200°C), similar to that obtained from fluid inclusion studies, as shown by Beaudoin and Pitre (2005). This range in temperature, however, does not explain all the variance in fluid $\delta^{18}\text{O}$ and δD values, as shown by the smaller quartz-tourmaline fractionation for heavier mineral compositions (Fig. 2B). This, in turn, yields the relation between fluid temperature and H-O isotope composition shown in Figures 2C and 4B.

The large range in fluid oxygen isotope composition of orogenic gold deposits has been ascribed to: 1) uncertainty in the temperature of equilibrium; 2) fractionation during “unmixing” by immiscibility or boiling; 3) fluid/rock reaction in the source or along fluid flow paths (Goldfarb et al., 2005). The detailed study of the Val-d’Or vein field shows that the effect of a temperature is a contributing factor to the oxygen isotope composition variance. Fluid boiling has little effect on the oxygen isotope composition, but has potential to significantly affect the hydrogen isotope composition below the critical temperature of the fluid, as shown in Figure 4B. Fluid/rock exchange contributes to the variance in oxygen isotope composition typical for orogenic gold deposits, as shown by numerical modeling for the Val-d’Or vein field by Beaudoin et al. (2006), but is not capable of causing the whole range in composition. A feature common to orogenic gold deposits is a small variance of oxygen isotope compositions at the deposit scale coupled to a larger variance between deposits in one district (Beaudoin and Pitre, 2005; Bierlein and Crowe, 2000; Gray et al., 1991). The Sigma deposit could represent an exception with a higher variance in $\delta^{18}\text{O}$ values, despite quartz-tourmaline oxygen isotope equilibrium across the range in values. Fluid/rock reactions only would require more than one distinct fluid sources and/or flow paths to uniquely imprint the oxygen and strontium isotope compositions of a deposit that is not consistent with the geology of the country rocks of orogenic gold deposits. The fluid/rock exchange hypothesis also requires specific combinations of isotopic compositions when multiple stable and radiogenic isotope systems are considered simultaneously, in order to yield the broad O-Sr covariation shown in Figure 8 for the Val-d’Or vein field, for example. Finally, the hydrogen and oxygen isotope compositions of tourmaline are not consistent with water-rock exchange because the heavier hydrogen and oxygen isotope compositions would

require very high atomic water-rock ratios (above 50) whereas even very low water-rock ratios (below 0.01) cannot yield fluids with δD as low as -40 (Val-d'Or) or -80 (Star Lake) without reaction with a δD value of less than -100‰.

The H, O, and Sr isotope compositions typical of orogenic gold deposits is better explained by a combination of water-rock reactions and mixing between fluids with different compositions and therefore sources. Fluid mixing has been proposed in a few orogenic gold vein field, including the Massif Central, France (Boiron et al., 2003), Omai, Guyana (Voicu et al., 1999), Wiluna, Australia (Hagemann et al., 1994), St. Ives, Australia (Neumayr et al., 2008) and Val-d'Or (Beaudoin and Pitre, 2005). Evidence for fluid mixing between surficial and metamorphic fluids has also been argued from fluid inclusion studies for the Massif Central (Boiron et al., 2003), although in the case of Wiluna, Hagemann and Lüders (2003) showed that the stibnite in the upper parts of the deposit formed by fluid immiscibility. Numerical modeling of fluid flow in fractured rocks of the Val-d'Or orogenic gold vein field (Beaudoin et al., 2006), showed water-rock reaction cannot explain the oxygen isotope isopleths in vein quartz and that mixing of two fluids was required to explain the $\delta^{18}O$ values of vein quartz. In St. Ives, the mineralogy suggests gold precipitated where two fluids of contrasting redox mixed (Neumayr et al., 2008). Fluid mixing, however, is not known in deeper-seated hypozonal orogenic gold deposits. Fluid mixing, as shown in these studies, most likely requires detailed district-scale documentation that is not available in most orogenic gold districts.

We consider that mixing of fluids from different reservoirs is an important mechanism to explain the range in stable and radiogenic isotope compositions documented in the Val-d'Or, and other orogenic gold deposits. Fluids originating from different reservoirs are likely to have other contrasting physico-chemical properties, such

as salinity, pressure, chemical composition, and temperature as shown for the Val-d'Or example. Mixing of fluids with contrasting composition can create conditions favourable for abrupt changes in gold solubility, leading to gold together with that of other vein minerals precipitation, such as shown by Neumayr et al. (2008), for example. Ridley and Diamond (2000) concluded that the composition of auriferous fluids in orogenic gold deposits reflects fluid-rock exchange along the fluid pathway, or a mixture of the signatures from the fluid source and the wallrocks, such that the fluid source would be masked. This implies only one fluid is involved in the formation of orogenic gold deposits, and imposes a low variance in isotopic composition. Instead, mixing of at least two hydrothermal fluids is a process that allows for the range in isotope compositions and temperatures documented in several orogenic gold districts (Beaudoin, 2011).

6. Conclusions

Quartz and tourmaline from the Val-d'Or orogenic gold vein field formed over a range of temperature (280-492 °C) and hydrothermal fluid $\delta^{18}\text{O}$ (2.8 to 9.3 ‰), δD (-35 to 30‰), and $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.70071 to 0.70225). The covariation of $\delta\text{D}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ with temperature, and with $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ of vein tourmaline indicates mixing between a low $\delta^{18}\text{O}$ (< 1.5 ‰), high δD (> -10 ‰), high $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (> 0.7022), low temperature (< 280 °C) upper crustal fluid, and a high $\delta^{18}\text{O}$ (> 9.3 ‰), low δD (< -40 ‰), low $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (< 0.7007), high temperature (> 490 °C) deep-seated metamorphic fluid. The high δD values of the upper crustal fluid are likely a consequence of open system mineral-water and liquid-vapour fractionation in the fluctuating pressure, dynamic hydrothermal system, that formed the orogenic gold vein field in Val-d'Or. The low $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (<0.7007) of the deep-seated metamorphic fluid end-member is consistent with Archean (ca 2.7 Ga)

prograde metamorphic dewatering of typical volcanic and sedimentary country rocks of the Val-d'Or area. The higher $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (>0.7022) of the upper crustal fluid most likely resulted from a long history of water-rock exchange between Archean seawater and carbonate as well as plutonic rocks of the Abitibi sub-province.

This study suggests that the Val-d'Or orogenic gold veins formed by mixing of two fluid end-members, metamorphic and supracrustal, without any significant contribution from magmatic or mantle fluid components. The H-O-Sr isotope compositions of vein minerals indicate that the fluids were sourced from a crustal segment, similar to the local country rocks, and undergoing prograde metamorphism during burial in an accretionary setting. The buoyant deep-seated metamorphic fluid rose into crust to the brittle-ductile crustal transition where it mixed with descending upper crustal fluids derived from Archean seawater that had been trapped into the country rocks porosity.

The range in H, O, Sr isotope compositions in the Val-d'Or vein field is not unlike that found in other orogenic gold districts (Kerrick, 1987, Beaudoin, 2011). The coupled isotopic covariations described in the Val-d'Or vein field, shown here to be a consequence of mixing upper crustal and metamorphic fluids, most likely represent a common context during the formation orogenic gold deposits.

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Figure Captions

Figure 1. Regional geology map of the Val-d'Or orogenic gold vein field showing the location of the quartz-tourmaline-carbonate and quartz-carbonate veins studied (modified from Beaudoin and Pitre, 2005).

Figure 2. A) Plot of $\delta^{18}\text{O}$ values of quartz versus coexisting tourmaline in orogenic gold veins of the Val-d'Or vein field. Isotherms computed using Kotzer et al. (1993). Sample 96-DP-15 contains intergrown quartz such that tourmaline has a higher $\delta^{18}\text{O}$ that is not in oxygen isotope equilibrium with quartz (Table 1). B) Plot of $\delta^{18}\text{O}$ values for quartz and tourmaline versus the difference in composition $\Delta_{\text{qz-tur}}$. C) Plot of quartz-tourmaline oxygen isotope equilibrium temperature using Kotzer et al. (1993), versus the oxygen isotope composition of H_2O computed using quartz and tourmaline $\delta^{18}\text{O}$ values (Table 1).

Figure 3. Variation of $\delta^{18}\text{O}_{\text{qz,tur}}$, $\delta\text{D}_{\text{tur}}$, quartz-tourmaline oxygen isotope temperature of equilibrium, and $^{87}\text{Sr}/^{86}\text{Sr}_{(\text{i})}$ with respect to sample depth below surface for the Sigma deposit (Table 1).

Figure 4. A) δD versus $\delta^{18}\text{O}$ diagram showing the composition of tourmaline from Val-d'Or and the Trans-Hudson Orogen, Canada (Ansdell and Kyser, 1992; Fedorowich et al., 1991; He, 1998; Hrdy and Kyser, 1995; Ibrahim and Kyser, 1991; Schultz, 1996) and compute composition of water using Kotzer et al. (1993), with reference to natural water reservoirs (Sheppard, 1986). B) Diagram of $\delta\text{D}_{\text{H}_2\text{O}}$ versus the temperature of quartz-tourmaline oxygen isotope equilibrium. The vertical line shows the critical temperature of

water, low salinity solutions critical temperatures are higher. The vertical arrow show the liquid-vapour fractionation of 2m NaCl solutions at 350 °C (Horita et al., 1995).

Figure 5. Histogram of $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ for vein carbonate and computed at 2.7 Ga from Rb, Sr and measured $^{87}\text{Sr}/^{86}\text{Sr}$ (Tables 1 and 2) for vein tourmaline, scheelite, and other minerals, and for whole rocks from the Val-d'Or area. Initial Sr isotope composition from literature for Abitibi and Yilgarn scheelite (Bell et al., 1989; Mueller et al., 1991), and for tourmaline and other minerals (actinolite and piemontite) from the Val-d'Or and the Abitibi sub-province (Kerrick et al., 1987; King and Kerrich, 1989). BABI: Basaltic Achondrite Best Initial (Faure, 1986).

Figure 6. Diagrams of $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ in relation to the Rb and Sr content. A) $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ vs $1/\text{Sr}$, and B) $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ vs Rb/Sr, for tourmaline (this study) divided by the temperature of oxygen isotope equilibrium between quartz and tourmaline (Table 1). C) $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ vs $1/\text{Sr}$, and D) $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ vs Rb/Sr, for regional country rocks of the Val-d'Or orogenic gold vein field (Table 2).

Figure 7. A) $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ vs $1/\text{Sr}$, and B) $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ vs Rb/Sr, for tourmaline (this study) and from literature for Abitibi and Yilgarn scheelite (Bell et al., 1989; Mueller et al., 1991), and for other minerals (actinolite and piemontite) and tourmaline from the Val-d'Or orogenic gold vein field and the Abitibi sub-province (Kerrick et al., 1987; King and Kerrich, 1989).

Figure 8. Diagram of tourmaline $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ vs $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, with model mixing lines between two fluid end-member compositions, computed for fluids with different [upper crustal : metamorphic Sr] concentration ratios (Banner and Hanson, 1990). Data are divided according the 350°C temperature of quartz-tourmaline oxygen isotope equilibrium (Table

1). Typical rock sources in the Abitibi sub-province, with high and low Sr content and isotope ratios are discussed in the text.

Table 1. Quartz and tourmaline composition from the Val-d'Or orogenic gold deposits.

Deposit	Number	Sample	Longitude	Latitude	Quartz	Carbonate	Tourmaline						T	H ₂ O	
	(Fig. 1)				$\delta^{18}\text{O}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{18}\text{O}$	δD	Sr	Rb	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$	(Qz-Tur)	$\delta^{18}\text{O}$	δD
					VSMOW (‰)		VSMOW (‰)	VSMOW (‰)	ppm	ppm		t=2.7 Ga	°C	VSMOW (‰)	VSMOW (‰)
Akasaba	1	96-DP-69	-77.5622	48.0456	11.1		7.5	-36	367	0.10	0.702134	0.702103	285	3.7	23
Audet	2	96-DP-50	-77.7254	48.0995	11.2		8.6	-13	122	0.14	0.702132	0.702002	400	7.1	19
Beaufor	3	96-DP-151	-77.5557	48.1601	10.6	0.702060	7.0	-36	584	0.04	0.701449	0.701441	285	3.2	23
		96-DP-162			10.8	0.701559	8.4		935	0.10	0.701514	0.701502	432	7.4	
Buffadison	4	96-DP-67	-77.4375	48.0902	10.5	0.701912	7.9		280	0.16	0.702093	0.702029	400	6.4	
Canmet	5	96-DP-189	-77.5647	48.0964	10.3		6.7	-30	258	1.11	0.701935	0.701449	285	2.9	29
Canmet-Nord	6	96-DP-208	-77.5691	48.1044	10.0		6.7	-35	273	0.22	0.702337	0.702246	313	3.6	16
Découverte	7	96-DP-83	-77.7646	48.1048	11.3		8.2		268	0.02	0.701544	0.701535	334	5.6	
Dumont	8	96-DP-	-77.6797	48.1257	10.5		8.2	-29	291	9.52	0.704409	0.7007	451	7.4	-5

		10													
Goldex	9	96-DP-178	-77.8740	48.0905	11.3	0.701767	8.3	-31	536	0.05	0.701241	0.701230	346	5.9	12
Louvicourt Goldfields	10	96-DP-15	-77.5649	48.0613	12.0		11.4*	-49	49	0.10	0.701806	0.701575			
		96-DP-16			11.7	0.701832	9.5						470	9.0	
Lucien- Béliveau	11	96-DP-59	-77.5164	48.1393	11.4		8.1	-54	257	0.03	0.701527	0.701514	313	5.0	-3
Nord-Ouest	12	96-DP-55	-77.6965	48.1254	10.4		7.7		239	0.34	0.701542	0.701381	358	5.5	
Shawkey		96-DP-44	-77.8894	48.1135				-34							
Sigma**	13	1128Mz one9	-77.7575	48.0983	11.3		7.6	-69	469	2.55	0.701945	0.70133	280	3.6	-8
		1128Sto pe1			11.5		8.1	-47	330	0.32	0.701887	0.701777	303	4.8	7
		1128WF lat#7			9.8										
		1426WA			12.5		8.9	-52	296	0.02	0.701540	0.701532	285	5.1	7
		1491W# 9			10.8		8.6	-45	217	0.16	0.701804	0.701721	470	8.1	-24

		14L- Xcut#32			11.1										
		18L- Raise#9			9.7										
		1821W# 3			10.5										
		2321Sto pe#1			11.0										
		23L- Xcut#12			11.0		8.9	-52	155	0.01	0.701402	0.701394	492	8.6	-34
		2502WS tope#10			12.6										
		3102ESt ope#4			12.0										
		32L- XCut19			11.4		8.4	-44	316	0.04	0.701512	0.701497	344	5.9	-1
		Duplicat e							404	0.02	0.701458	0.701453			
Sigma-2	14	96-DP- 218	-77.4598	48.0663	11.7		9.6		304	0.05	0.701733	0.701714	492	9.3	
Siscoe	15	96-DP- 22	-77.8627	48.1411	12.0		8.9	-42	136	0.04	0.701457	0.701424	334	6.3	4

Sleepy Lake	16	96-DP- 120	-77.4009	48.0554	9.2		6.8	-25	542	0.06	0.701404	0.701392	432	5.8	2
Wrightbar	17	96-DP- 139-5	-77.5794	48.0948	9.8		6.5		423	0.02	0.701753	0.701748	313	3.4	

*: tourmaline concentrate contains quartz detected by XRD. **: Sigma deposit samples first 2 digits multiplied by 100 give depth of level in feet (e.g., 32L-XCut19 is 3200 feet below surface). Quartz and tourmaline $\delta^{18}\text{O}_{\text{VSMOW}}$ values in bold from Beaudoin et Pitre (2005). Equilibrium temperature using Kotzer et al. (1993). H_2O $\delta^{18}\text{O}_{\text{VSMOW}}$ and $\delta\text{D}_{\text{VSMOW}}$ values computed using temperature from Kotzer et al. (1993) and the quartz- H_2O fractionation (Matsuhisa et al., 1979) and the tourmaline- H_2O fractionation of Kotzer et al. (1993).

Table 2. Sr, Rb, and Sr isotope composition of country rocks from the Val-d'Or area.

Rock	Sample	Longitude	Latitude	Sr	Rb	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}_{(t)}$
				ppm	ppm		t = 2.7 Ga
Bourlamaque	YG-07-103	-77.5474	48.1446	185	43	0.726017	0.6997
Batholith (granodiorite)	YG-88-62	-77.6698	48.1589	227	44	0.722362	0.7004
Bevcon	96-DP-65	-77.4375	48.0902	122	16	0.714642	0.6998
Pluton (granodiorite)	YG-52-146	-77.4057	48.0938	160	23	0.717128	0.7009
Sullivan	YG-43-75	-77.6643	48.0695	1324	198	0.704961	0.6881
Pluton (granodiorite)	YG-35-59	-77.7086	48.0785	234	20	0.706177	0.6965
Andesite	YG-56-140	-77.4192	48.0589	218	6	0.715986	0.7129
	YG-46-24	-77.8459	48.0826	156	8	0.710201	0.7044
Basalt	96-DP-95	-77.5602	48.0470	60	109	0.891088	0.682
	YG-71-35	-77.7846	48.1433	295	8	0.706154	0.70309
	YG-82-47	-77.7402	48.1728	101	11	0.712125	0.6998
Komatiite	YG-18-23	-77.8396	48.1019	12	1	0.709332	0.6999
	YG-24-37	-77.7826	48.0842	27	3	0.712736	0.7002
	YG-2-104	-77.5454	48.1223	< 2	< 1	0.737471	-
Grauwacke	96-DP-05B	-77.7023	48.0442	817	38	0.706978	0.7017
	YG-12-128	-77.4641	48.1425	175	21	0.714007	0.7004
	YG-60-16	-77.8953	48.0763	353	82	0.727746	0.7014

Figure

Figure 1. Beaudoin & Chiaradia (2015)

Figure 2. Beaudoin & Chiaradia (2015)

Figure 3. Beaudoin & Chiaradia (2015)

Figure 4. Beaudoin & Chiaradia (2015)

Figure 5. Beaudoin & Chiaradia (2015)

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