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

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

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 δ18O 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 (87Sr/86Sr(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, form 0.701243 to 0.703641. A series of samples from the Sigma deposit displays no systematic variation with depth for δ18O values of quartz or tourmaline, δD values of tourmaline, temperature of equilibrium, or 87Sr/86Sr(i). The 87Sr/86Sr(i) of local komatiite, basalt, andesite, grauwacke and granodiorite, at 2.7 Ga, ranged from 0.681971 to 0.7128706. Country rocks with low 87Sr/86Sr(i) are likely a consequence of hydrothermal resetting of the Rb/Sr system in these samples.

Covariation of the calculated equilibrium δDH2O and δ18OH2O with quartz-tourmaline equilibrium temperatures indicates mixing between a low-δ18O (< 1.5 ‰), high δD (> -10 ‰), low temperature (< 280 °C) upper crustal fluid, and a high-δ18O (> 9.3 ‰), low δD (< -40 ‰), high temperature (> 490 °C) deep-seated metamorphic fluid. At temperatures below the critical point for low-salinity hydrothermal fluids, δDH2O are affected by liquid-vapour phase separation, yielding the high δD values characteristic of the upper crustal fluid. A broad covariation between δ18OH2O and the 87Sr/86Sr(i) of tourmaline is consistent with mixing of two fluids from two reservoirs with different Sr concentrations and δ18OH2O values. The low 87Sr/86Sr(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 87Sr/86Sr(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.
Québec, May 1st 2016

Dear Dr. Böttcher,

Thank you for the constructive review of our submission to Chemical Geology entitled "Fluid mixing in orogenic gold deposits: evidence from the H-O-Sr isotope composition of the Val-d'Or vein field (Abitibi, Canada)". We have revised the submission according to the suggestions by the referee. In the following paragraphs, we include the original comments and the actions taken, or our response to the comments by the referees, our response being in red. The new submission contains a version with track changes, and a version without them. We hope these change adequately respond to the reviewer’s comments.

Best regards,

Georges Beaudoin,
Géo, Ph.D.
Professeur
Chaire de recherche industrielle CRSNG—
Agnico-Eagle en exploration minérale
Département de géologie et de génie géologique
1065, rue de la Médecine
Québec (Québec) G1V 0A6
CANADA
Fluid mixing in orogenic gold deposits: evidence from the H-O-Sr isotope composition of the Val-d'Or vein field (Abitibi, Canada)

Response to review #2 (in red).

Reviewer #2: In my first review, I noted three major concerns about the analysis of the data and noted that these should be countered or addressed before publication. I here re-examine these concerns in view of the revisions of the manuscript and the authors’ commentary.

(Line numbers refer to the version of the text that contains the edits.)

Oxygen isotope thermometry:
Addition of uncertainty bars to Figures 2A and 2B has clarified the analysis somewhat - although I note that the bars in 2A need modification to take into account the different vertical and horizontal scales in the figure. The statement added to line 226 is however misleading. The expected range (at 1 sigma) for the data is 0.6 ‰, hence 1/3 the measured range, not 1/6. This sentence should be rephrased.
Figure 2A corrected. Range corrected.

From the response, it seems however that the authors missed an aspect of my concern about the presentation of the oxygen isotope data. I did not have a concern that they had demonstrated variability of <delta>18O H2O. I remain unconvinced however that the trend in Figure 2C has been demonstrated with statistical confidence. Because <DELTA>18Oqtz/tur-H2O is a function of T in all fractionation equations, if we have a set of <delta>18Oqtz values and assign each a different T, we will generate linear <delta>18O H2O - T relationships. Figure 2B is critical to resolve whether a true relationship can be demonstrated from this data set, but no statistical analysis of the data is given. Visual examination does not convince me of that there is a statistically significant relationship between <delta>18Oqtz or <delta>18Otur and <DELTA>18Oqtz-tur as is claimed in line 224 and following.

As described in the text, Figure 2C shows both the empirical fractionation (∆ Qz-Tur), and the derived temperature of equilibrium. Of course T depends on ∆ Qz-Tur, and fluid on both the previous and δQz or δTur. But, as indicated in text, the fluid composition is computed from the mineral water fractionation for both quartz and tourmaline. Each of these equations has a unique relation between T and ∆ Qz-Tur. Each mineral yields like T-δ18O relationships, albeit offset by errors in the calibration, as described in the text. It is actually remarkable that both Qz and Tur give the same fluid composition variations.

The second point of the referee is about the statistical analysis of the data. The problem is that the referee does not provide information about what statistical test we should
apply on data in Figure 2B. We only describe the general distribution of data in the $\delta$-$\Delta$ space. This is then used to compute $T$ and fluid values using independent equations (Qz-H$_2$O, Tur-H$_2$O, Qz-Tur). This is where we make useful interpretations, and the referee agrees that « Figure 2C has been demonstrated with statistical confidence ».

Part of my concern here is also whether 1 sigma or 2 sigma is the most appropriate measure of analytical uncertainty for the interpretations made in the paper, specifically of whether temperature was variable. What level of confidence is appropriate to support a model? The question could perhaps usefully be rephrased here as - what level of confidence is needed to support a model that is suggested as a possible explanation and what is needed for a 'demonstrated' model? The language of the paper as it currently stands is the latter. The word 'demonstrates' is used in line 637 for instance, but isn't this too strong? I am not saying that a re-evaluation of the model is required, rather that it should be presented as the preferred model and not as if proven beyond all reasonable doubt.

Typically, light stable isotopes have been reported at the 1sigma level of confidence. We follow here.

It is all a question of appreciation, the words that are used. We did not infer «proven beyond all reasonable doubt » as implied by the referee, and we used terms such as « most likely » in many instances. We have replaced « demonstrates » by « suggests ».

The same criticism about word choice applies to some of the wording which presents earlier work, e.g. line 586, 'proposed' would be better than 'documented'. Corrected.

Strontium initial isotope ratios:
My concern here was not the effect of uncertainty of age on Sr(i) - the authors correctly note that these uncertainties will have insignificant affect. The concern is more the quoting and using of calculated ratios that are lower than depleted mantle at 2.7Ga. These can not be real initial values. Lahaye and Arndt (1996) report similar calculated values and argue (in their case) that they are the result of Grenvillean age alteration. Invoking later alteration is likely appropriate here. My recommendation is to present the data in a table, note that values < 0.7002(?) indicate later alteration, and do not include these values in Figure 5 or in any description or discussion. (Values higher than the cut-off could also be altered, but we have no way of filtering these). This change would be cosmetic and would not affect your interpretations and conclusions, but is important to forestall potential misunderstanding by readers.
We added that these values below BABI are not discussed further in L 494. On Figure 5, we prefer to leave the data in the histogram but indicate the range for which values are below BABI are affected by open system alteration.

Hydrogen isotope values:
The trigger for my concern here was that the $<\delta^{2}H\text{H}_{2}O$ values are so unusual (especially for higher temperature hydrothermal waters) and hence should be discussed with their near uniqueness in mind, and the uniqueness should be clearly stated. The compilation of Taylor (in Barnes 1997) shows nothing similar (cf. line 645). Ideally, all possible explanations of the unusual results should be presented and discussed, including that the data is not a robust measure of the composition of the ore forming fluid. Likely uncertainties and shortcomings of the data should be noted.

Taylor (1997) is a very succinct discussion of some of the data on orogenic gold deposits. It does not report the full width of orogenic gold $dD$ values. Our paper compares the composition of tourmaline from previous studies, to our knowledge, all previous Tur $\delta D$ values are reported. The values are similar to previous studies, but tend to the higher side. This is not laboratory bias as the $\delta D$ have been done in Kyser's lab, from which most previous data also comes from. In addition, Beaudoin (2011) reported a compilation of stable isotope compositions in orogenic gold deposits. The $\delta O-\delta D$ plot is below:
It shows that contrary to the opinion of the reviewer, the $\delta$D values of tourmaline in Val-d’Or are not particularly special. The inference that the reviewer makes about the robustness of tourmaline $\delta$Dis not substantiated by any data. We are at loss to discuss it, as this mineral has been used in many studies without evidence of any particular issue.

Ideally all possible processes that could potentially give rise to the $<$delta$>$2HH2O range and values should be presented and then discussed, in order to demonstrate that the proposal here is the most likely. Essentially I am arguing for restructuring of the
presentation on this data (together with some elaboration of arguments) in order to allow
the reader to better assess the interpretation you give.
This section is rewritten entirely in L404-431 in R2. Temperature and Rayleigh
fractionation are described and discussed in separate paragraphs. A supportive figure
could be added, but is not required in our opinion. A draft version is below for your
consideration, should you request its incorporation into the paper.

Minor textual points:
Line 30 - 32. Word missing in sentence? In any case more precise would be 'Coexisting
quartz and tourmaline… have oxygen isotope fractionation indicating equilibration over
a range of temperature (280 - 492 °C ± **)'.
Modified as suggested.

Line 72. Word missing?
Sentence verified, but no missing words identified.

Line 120 + 598. Neumayr
Corrected.

Lines 125 and 130 - ages given are not exactly equivalent.
The L130 sentence starts by referring to dykes cross-cutting viens. The ages known for
these instances are not as numerous at the whole range of dyke ages referred on L125.

Line 235 subscript Qz-Tur
Done in whole paragraph and elsewhere.

Line 242 and following. In most cases, 'isotope fractionation' should replace 'isotope equilibrium'.

We disagree. We refer to the temperature of isotope equilibrium, which is computed from the isotope fractionation.

Line 268 - 270. The information on the age of gold mineralisation should be transferred to the discussion on geochronology at the beginning of section 2.1.

We believe it is better to keep the age information here because it justifies the value used to compute the Sr(i).

Line 322 and following + line 571. Your data here shows that the conclusion of Beaudoin and Pitre (2005), that there is limited variance in a deposit, no longer holds in all cases. These sentences need rewording to tell the reader that the earlier conclusion no longer holds.

On L322, we describe at length the variance in δO at the Sigma mine. In deposits studied in detail by Beaudoin and Pitre (2005), we showed the variance of data in one deposit was similar to analytical uncertainty. The new data for the Sigma deposit shows a larger variance, but we cannot find a relation to obvious parameters (depth, for example), as stated in the text.

We added a sentence (L328) giving the average of all Sigma analyses: «Combining the results of this study with those of Beaudoin and Pitre (2005) and Olivo et al. (2006), the average δ18O value for the Sigma deposit is 11.2±0.7 ‰ (n= 26).” We also added a mention at the end of the paragraph that despite the range, the Qz-Tur pairs are in isotope equilibrium.

We disagree. We refer to the temperature of isotope equilibrium, which is computed from the isotope fractionation.

The fact that the variance is low in general is not negated by the new value at Sigma. In previous studies, cited at L571 of R1, the deposit variance values are not reported, so a discussion of the issue is difficult (values are not tabulated in Gray et al., so one cannot reprocess the data). There we do not imply the variance is smaller than analytical uncertainty, we only qualify it as small, as done in other previous work. We suggest to add a sentence to highlight the special case of the Sigma deposits on L602 (R2): “The Sigma deposit could represent an exception with a higher variance in δ18O values, despite quartz-tourmaline oxygen isotope equilibrium across the range in values.”

Line 379. Most water-mineral H isotope fractionation curves have kinks such that the
fractionation does not uniformly increase to lower temperatures. Not true for the Tur-water fractionation. Brucite, clays do, not mica or hornblende.

Paragraph starting line 387 + line 586. The critical point of 2m NaCl is ~ 480 °C. What explanation is there of why the change in behaviour is recognised either side of Tcritical for pure water? Is this the temperature of maximum liquid-vapour isotope fractionation?

This is a good point. The text is modified to refer to Ridley and Diamond (2000) inclusion fluids salinity being mostly between 3 and 7 wt.% NaCl eq., and which is more close to 1m NaCl, and for which the CP of saline water is near 425°C. The discussion thereafter is modified to use the value for the 1m l-v maximum fractionation of -5‰ at 320°C (based on Horita et al.).

Lines 460 - 471. What is meant by 'similar Sr content'? The model trajectories in Figure 8 are for Sr concentration ratios varying by a factor of 200. This is surely a significant range, especially when compared to the data given in lines 513-524. This sentence is removed since the tourmaline Sr content varies from 49 to 935 ppm. A sentence is added at the end of the paragraph (L527): 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).

Line 508. It would be worth noting that the values for carbonate overlap bulk Earth at end Archean. This is true for all the potential source rocks discussed in this paragraph. We do not see what it brings to the discussion.

Line 600. This sentence would more precisely express the idea if it stated that it is the volume of data that indicates fluids mixing. We are not sure what is meant here. The sentence on L600 suggests that detecting mixing requires detailed district-scale documentation that is not available in most gold districts. It is not the volume, but the detailed description that is important.

Line 638. This is the only mention of magmatic and mantle fluids. Could be deleted without loss. Instead, we prefer to state the metamorphic and supracrustal fluid origins, to emphasize lack of evidence for magmatic/mantle sources.

Figure 1. Overlapping text needs correction. Corrected. That happened in the pdf generation by the system.

Figure 4. The theoretical $<\Delta DL>V$ is at most 17 ‰, not 45 ‰ as implied in the figure. Modification is required. Verified the arrow was equal to 17‰, not 45‰. Modified to make the arrow length equal to the 5‰ fractionation for 1m NaCl at 320°C, in accord with modifications following response to the referee’s comments above.

Figure 5. This figure would be much improved if redrafted with bars below and above the axis - rocks below, hydrothermal minerals above. We have looked into this suggestion. We can implement it but the disadvantage is that the tick marks and values for the bins will be overlapped by the rock value bars.
Graphical Abstract

Figure 8. Beaudoin & Chiaradia (2015)
Highlights

- Coupled H-O-Sr isotope composition of tourmaline and quartz documented
- Val-d'Or orogenic gold deposits formed by mixing of two fluids
- Supracrustal fluid: T < 280º C, δ¹⁸O < 2.8 ‰, δD > -10 ‰, ⁸⁷Sr/⁸⁶Sr(i) > 0.7022
- Deep-seated fluid: T > 490º C, δ¹⁸O > 9.3 ‰, δD < -40 ‰, ⁸⁷Sr/⁸⁶Sr(i) < 0.7007
Fluid mixing in orogenic gold deposits: evidence from the H-O-Sr isotope composition of the Val-d’Or vein field (Abitibi, Canada)

Georges Beaudoin (corresponding author)
Département de géologie et de génie géologique, Université Laval, Québec (Qc) Canada G1X 4X4 (beaudoin@ggl.ulaval.ca; 1-418-656-3141)

Massimo Chiaradia
Section des Sciences de la Terre et de l’Environnement, Université de Genève, Genève, Switzerland CH-1205

Revised version for submission to Chemical Geology

21 April 2016
Highlights

- Coupled H-O-Sr isotope composition of tourmaline and quartz documented
- Val-d’Or orogenic gold deposits formed by mixing of two fluids
- Supracrustal fluid: T < 280ºC, \(\delta^{18}O < 2.8 \, \text{‰}, \delta D > -10 \, \text{‰} \), \(87\text{Sr}/86\text{Sr} > 0.7022\)
- Deep-seated fluid: T > 490ºC, \(\delta^{18}O > 9.3 \, \text{‰}, \delta D < -40 \, \text{‰} \), \(87\text{Sr}/86\text{Sr} < 0.7007\)

Abstract

Quartz and tourmaline from the Val-d’Or, Québec (Canada) orogenic gold vein field are have oxygen isotope fractionation indicating equilibrium over a range of temperature (280-492 ºC) and have a The range of \(\delta^{18}O\) 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 \((87\text{Sr}/86\text{Sr})\) 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, form 0.701243 to 0.703641. A series of samples from the Sigma deposit displays no systematic variation with depth for \(\delta^{18}O\) values of quartz or tourmaline, \(\delta D\) values of tourmaline, temperature of equilibrium, or \(87\text{Sr}/86\text{Sr}\). The \(87\text{Sr}/86\text{Sr}\) of local komatiite, basalt, andesite, grauwacke and granodiorite, at 2.7 Ga, ranged from 0.681971 to 0.7128706. Country rocks with low \(87\text{Sr}/86\text{Sr}\) are likely a consequence of hydrothermal resetting of the Rb/Sr system in these samples.

Covariation of the calculated equilibrium \(\delta D_{\text{H}_{2}O}\) and \(\delta^{18}O_{\text{H}_{2}O}\) with quartz-tourmaline equilibrium temperatures indicates mixing between a low-\(\delta^{18}O\) (< 2.81.5 ‰), high \(\delta D\) (> -130 ‰), low temperature (< 280 ºC) upper crustal fluid, and a high-\(\delta^{18}O\) (> 9.3 ‰), low \(\delta D\) (< -40 ‰), high temperature (> 490 ºC) deep-seated metamorphic fluid.
At temperatures below the critical point for low-salinity hydrothermal fluids, $\delta D_{\text{H}_2\text{O}}$ are affected by liquid-vapour phase separation, yielding the high $\delta D$ values characteristic of the upper crustal fluid. A broad covariation between $\delta^{18}O_{\text{H}_2\text{O}}$ 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 $\delta^{18}O_{\text{H}_2\text{O}}$ 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 (D₁). 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 (D₂) 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 (D3) along the CLLTZ (Robert et al. 1995; Neumayer et al. 2000). D2 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 $\delta^{18}O$ values, however, was shown for different deposits. The samples
selected for this study are representative of the range in $\delta^{18}O$ 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 $\delta$-notation relative to V-SMOW with a precision better than 0.2‰ ($\sigma$). Accuracy and
precision of $\delta^{18}O$ 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 $\delta$-notation relative to V-SMOW with
a precision better than 2‰ ($\sigma$).

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 HNO3, 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 (2σ).

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 (\(^{84}\text{Kr}\)), 86 (\(^{86}\text{Kr}\)) and 87 (\(^{87}\text{Rb}\)) were corrected by monitoring \(^{83}\text{Kr}\) and \(^{85}\text{Rb}\). 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 $\delta^{18}$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 $\delta^{18}$O–$\delta^{18}$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 $\delta^{18}O$ value of
quartz, and the quartz-H$_2$O fractionation of Matsuhisa et al. (1979), the $\delta^{18}O$ of water in
equilibrium with quartz is estimated to have varied from 2.8 to 9.3 ‰ (Table 1).

The $\delta^{18}O$ values of coexisting quartz and tourmaline are plotted in Figure 2B
against the oxygen isotope fractionation between coexisting quartz and tourmaline ($\Delta_{Qz-Tur}$). Figure 2B shows that smaller $\Delta_{Qz-Tur}$ values are associated with higher tourmaline
$\delta^{18}O$ values, and that larger $\Delta_{Qz-Tur}$ values characterise tourmaline with lower $\delta^{18}O$ values.

The range in $\Delta_{Qz-Tur}$ values (1.8 ‰) is 6.3 times larger that the uncertainty of ±0.3 ‰ (Fig.
2B). Figure 2C is a plot of $\Delta_{Qz-Tur}$ values or the temperature of quartz-tourmaline oxygen
isotope equilibrium, using Kotzer et al. (1993), versus the $\delta^{18}O_{H_2O}$ computed from $\delta^{18}O_{Qz}$
and the fractionation of Matsuhisa et al. (1979), and from the $\delta^{18}O_{Tur}$ and the fractionation
of Kotzer et al. (1993). Because of the difference in the calibration of the fractionations,
the $\delta^{18}O_{H_2O}$ 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-$\delta^{18}O$ end-member, and a high-temperature, high-$\delta^{18}O$ end-
member (Fig. 2C). The $T-\delta^{18}O_{H_2O}$ relation reflects the fact that the smaller $\Delta_{Qz-Tur}$ values,
or higher temperatures, are associated with higher $\delta^{18}O_{Tur}$ values (Fig. 2B), or a heavier
fluid in terms of oxygen isotope composition. Conversely, larger $\Delta_{Qz-Tur}$ values (or lower
$T$) are associated with lower $\delta^{18}O_{Tur}$ 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 \(\delta^{18}O\) 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 \(\delta^{18}O\) values and lower equilibrium temperature (Fig. 3).

Tourmaline \(\delta D\) 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 \(\delta D_{\text{H}_2\text{O}}\) values in equilibrium with tourmaline have a range from -34 to 29‰ (Table 1). The tourmaline \(\delta D\) and \(\delta^{18}O\) 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 \(\delta D\) of -34‰ and a higher \(\delta^{18}O\) of 7.6‰, and the second with a higher \(\delta D\) of 29‰ and a lower \(\delta^{18}O\) 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 \(\delta D_{\text{H}_2\text{O}}\) (-34 ‰) at high temperature, and higher \(\delta D_{\text{H}_2\text{O}}\) (19 ‰) at 400 °C (Fig. 4B). At temperatures lower than 400°C, the linear relation is broken and the \(\delta D\) values of water are more variable and 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 0.047x10^{-3} to 5.437x10^{-3}, with one value at 32.715x10^{-3}. The $^{87}$Sr/$^{86}$Sr ratios are from 0.701241 to 0.704409 (Table 1). The initial Sr isotope compositions ($^{87}$Sr/$^{86}$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 $^{87}$Sr/$^{86}$Sr$_{(i)}$ reported in Table 1. At the Sigma deposit, the six samples show no systematic variation in $^{87}$Sr/$^{86}$Sr$_{(i)}$ with depth (Fig. 3). The variation in $^{87}$Sr/$^{86}$Sr$_{(i)}$ correlates neither with 1/Sr (the highest 1/Sr has near average $^{87}$Sr/$^{86}$Sr$_{(i)}$ ;Fig. 6A), nor with Rb/Sr (Fig. 6B). The sample with the highest Rb/Sr has the lowest $^{87}$Sr/$^{86}$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 $^{87}$Sr/$^{86}$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 $^{87}$Sr/$^{86}$Sr ranging from 0.701243 to 0.703641, excluding one value at 0.709624. The $^{87}$Sr/$^{86}$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 ppm Rb (Table 2). Komatiitic rocks have up to 27 ppm Sr, and less than 3 ppm 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 $1/\text{Sr}$ (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 δ¹⁸O 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 δ¹⁸O values have a variance, at the deposit-scale, which is similar to the analytical precision (± 0.2 ‰). Quartz δ¹⁸O 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 δ¹⁸O 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 $\delta^{18}$O$_{Qz,Tur}$ 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 $\delta^{18}$O values, or from 1.5 to 7.6 ‰ using tourmaline $\delta^{18}$O values, and the quartz-tourmaline equilibrium temperature (Table 1). The difference in $\delta^{18}$O$_{H2O}$ 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 $\delta^{18}$O values and using the assumption of isothermal conditions at 350 ºC.

The covariation of $\delta^{18}$O$_{H2O}$ 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 $\delta^{18}$O (Fig. 2B).

Quartz and tourmaline yield similar values for $\delta^{18}$O$_{H2O}$ 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-$\delta^{18}$O (< 1.5 ‰) fluid end-member had a lower temperature (<280 ºC) than the high-$\delta^{18}$O (>9.3 ‰), hydrothermal fluid end-member ($T > 492$ ºC; 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;
and extend the range towards higher $\delta$D 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 $\delta$D 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 $\delta$D 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 $\delta$D 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 $\delta$D values.

The composition of tourmaline precipitated from a fluid with a fixed composition ($\delta^{18}$O = 5 ‰; $\delta$D = 0 ‰), and along a temperature gradient from 500º to 300ºC, yields a trajectory of $\delta^{18}$O and $\delta$D values from 7.0 to 9.7 ‰ and from -17 to -55, respectively, not (Gregory et al., 1989) 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 δ\textsuperscript{18}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 δ\textsuperscript{18}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 x 10\textsuperscript{-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.

Figure 4B shows a plot of water hydrogen isotope composition in equilibrium with
tourmaline versus the temperature of equilibrium. Samples with temperatures of
equilibrium between 400 and 500ºC plot along a linear array. This array cannot result
from a temperature gradient since the depletion in D in tourmaline relative to water, as
for other hydrous silicates, increases at lower temperature. The higher δD values,
however, could result from a Rayleigh process wherein the hydrogen isotope
composition of the fluid is gradually enriched in D by precipitation of isotopically light
hydrous silicates, such as tourmaline, chlorite, muscovite or biotite, which have similar
ranges in δD values in orogenic gold deposits (Beaudoin, 2011). This linear array covariation of δD_{H2O} 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 can also be δD_{H2O} values is interpreted to record mixing between a high temperature (> 492 °C), low δD (<-40‰) 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_{H2O} and temperature is broken and δD_{H2O} values become more variable (Fig. 4B). This occurs at temperatures below the critical point of the low salinity (ca. 103-17 wt. % NaCl eq., or 2m NaCl; Horita et al., 1995) fluids typical of orogenic gold deposits (Ridley and Diamond, 2000)-(Goldfarb et al., 2005). 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 2m-1m NaCl solutions typical of orogenic gold deposits yields a maximum hydrogen isotope fractionation of -17.5 % at 350-320 °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 $\delta D$ 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 $\delta D_{\text{H}_2\text{O}}$ values below about 400 $^\circ$C (Fig. 4B).

The fact that $\delta D_{\text{H}_2\text{O}}$ 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, $\delta D_{\text{H}_2\text{O}}$ 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$^\circ$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 $\delta D_{\text{H}_2\text{O}}$ and $\delta^{18}O_{\text{H}_2\text{O}}$ values versus temperature are best explained by mixing of two main fluid end-member compositions. The low temperature (< 280 $^\circ$C), low $\delta^{18}O$ (< 1.5 ‰) and high $\delta D$ (> -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 $^\circ$C) best explain the variable, and high, $\delta D_{\text{H}_2\text{O}}$ values of the upper crustal fluid end-member. The high temperature (> 490 $^\circ$C),
high-δ\(^{18}\)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 \(^{87}\text{Sr}/^{86}\text{Sr}(\text{i})\) 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 \(^{87}\text{Sr}/^{86}\text{Sr}(\text{i})\) (Fig. 7B), such that the range in \(^{87}\text{Sr}/^{86}\text{Sr}(\text{i})\) is not a consequence of variation of the Rb content of tourmaline. Instead, the tourmaline \(^{87}\text{Sr}/^{86}\text{Sr}(\text{i})\) 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 \(^{87}\text{Sr}/^{86}\text{Sr}(\text{i})\) (0.70071 to 0.70225) must indicate that the auriferous hydrothermal fluids had the same range in strontium isotope composition.

The \(^{87}\text{Sr}/^{86}\text{Sr}(\text{i})\) 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 δ18O, high temperature fluid end-member was characterized by higher 87Sr/86Sr(i), whereas (ii) the deep-seated, metamorphic, low δD, high δ18O, high temperature fluid end-member had a less radiogenic Sr isotope composition (Fig. 8). The fact that tourmaline 87Sr/86Sr(i) plot near the vertical axis against 1/Sr indicates that the two fluids must have had similar Sr content (Fig. 6A). Lack of covariation between 87Sr/86Sr(i) and 1/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 87Sr/86Sr versus δ18O 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 87Sr/86Sr(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 ºC), high δD (>30 ‰), low δ18O (<1.5 ‰) but radiogenic 87Sr/86Sr(i) (>0.7023), whereas the second end-member hydrothermal fluid had a higher temperature (>490 ºC), low δD (<-40 ‰), high δ18O (<9.3 ‰) and non-radiogenic 87Sr/86Sr(i) (<0.7007).

5.3 Strontium sources

The Sr content and 87Sr/86Sr(i) of the Val-d’Or area country rocks indicate that volcanic and plutonic rocks have low Sr (<2 to 295 ppm) and 87Sr/86Sr(i) (0.6820 to 0.7009, and one high value of 0.7031), whereas sedimentary rocks have higher Sr (175-817 ppm) and 87Sr/86Sr(i) (0.7004 to 0.7014). The whole rock 87Sr/86Sr(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 87Sr/86Sr(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 87Sr/86Sr(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 87Sr/86Sr(i) values (0.7006 to 0.7031) (Davis et al., 2000; Verpaelst 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 87Sr/86Sr(i) metamorphic fluid. This interpretation is in contrast with that of Kerrich et al. (1987) and King and Kerrich.
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; Verpaelst 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 $^{87}\text{Sr}/^{86}\text{Sr}(\iota)$ 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 $\delta^D$, metamorphic fluid has low $^{87}\text{Sr}/^{86}\text{Sr}(\iota)$ 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 $\delta^{18}O_{\text{fluid}}$ (6.5‰), $\delta D_{\text{fluid}}$ (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 $\delta^{18}O$ and $\delta D$ 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 $\delta^{18}O$ and $\delta D$ 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...
The Sigma deposit could represent an exception with a higher variance in $\delta^{18}O$ 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 $\delta^D$ as low as -40 (Val-d’Or) or -80 (Star Lake) without reaction with a $\delta^D$ 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 documented 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 (Neumayer 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 $\delta^{18}O$ (2.8 to 9.3 ‰), $\delta D$ (-35 to 30‰), and $^{87}Sr/^{86}Sr_i$ (0.70071 to 0.70225). The covariation of $\delta D_{H_2O}$ and $\delta^{18}O_{H_2O}$ with temperature, and with $^{87}Sr/^{86}Sr_i$ of vein tourmaline indicates mixing between a low $\delta^{18}O$ (< 1.5 ‰), high $\delta D$ (> -10 ‰), high $^{87}Sr/^{86}Sr_i$ (> 0.7022), low temperature (< 280 °C), upper crustal fluid, and a high $\delta^{18}O$ (> 9.3 ‰), low $\delta D$ (< -40 ‰), low $^{87}Sr/^{86}Sr_i$ (< 0.7007), high temperature (> 490 °C) deep-seated metamorphic fluid. The high $\delta D$ 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 $^{87}Sr/^{86}Sr_i$ (<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 $^{87}Sr/^{86}Sr_i$ (>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 demonstrates suggests that the Val-d'Or orogenic gold veins formed by mixing of two fluid end-members, metamorphic and supracrystal, 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 (Kerrich, 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.

7. Acknowledgements

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research. Comments by Bruce Taylor and Andrea Dini improved significantly the paper.

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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 δ¹⁸O 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 δ¹⁸O that is not
in oxygen isotope equilibrium with quartz (Table 1). B) Plot of δ¹⁸O values for quartz and
tourmaline versus the difference in composition Δqz-tur. C) Plot of quartz-tourmaline
one oxygen isotope equilibrium temperature using Kotzer et al. (1993), versus the oxygen
isotope composition of H₂O computed using quartz and tourmaline δ¹⁸O values (Table 1).

Figure 3. Variation of δ¹⁸O_qz,tur, δD_tur, quartz-tourmaline oxygen isotope temperature of
equilibrium, and ^{87}Sr/^{86}Sr_i with respect to sample depth below surface for the Sigma
deposit (Table 1).

Figure 4. A) δD versus δ¹⁸O 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 δD_H₂O 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}Sr/^{86}Sr_i for vein carbonate and computed at 2.7 Ga from Rb,
Sr and measured ^{87}Sr/^{86}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 (Kerrich et al., 1987; King and Kerrich, 1989). **BABI: Basaltic**

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

Figure 7. A) \(^{87}\text{Sr}/^{86}\text{Sr}\) vs \(1/\text{Sr}\), and B) \(^{87}\text{Sr}/^{86}\text{Sr}\) 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 (Kerrich et al., 1987; King and Kerrich, 1989).

Figure 8. Diagram of tourmaline \(^{87}\text{Sr}/^{86}\text{Sr}\) 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.
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Table 1. Quartz and tourmaline composition from the Val-d'Or orogenic gold deposits.
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*: 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 δ18OVSOW values in bold from Beaudoin et Pitre (2005). Equilibrium temperature using Kotzer et al. (1993). H2O δ18OVSOW and δDVSMOW values computed using temperature from Kotzer et al. (1993) and the quartz-H2O fractionation (Matsuhisa et al., 1979) and the tourmaline-H2O fractionation of Kotzer et al. (1993).
Table 2. Sr, Rb, and Sr isotope composition of country rocks from the Val-d’Or area.

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<th>Rock</th>
<th>Sample</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Sr ppm</th>
<th>Rb ppm</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr})</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr}) (t = 2.7 Ga)</th>
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Fluid mixing in orogenic gold deposits: evidence from the H-O-Sr
isotope composition of the Val-d’Or vein field (Abitibi, Canada)

Georges Beaudoin (corresponding author)
Département de géologie et de génie géologique, Université Laval, Québec (Qc)
Canada G1X 4X4 (beaudoin@ggl.ulaval.ca; 1-418-656-3141)

Massimo Chiaradia
Section des Sciences de la Terre et de l’Environnement, Université de Genève, Genève,
Switzerland CH-1205

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Highlights

- Coupled H-O-Sr isotope composition of tourmaline and quartz documented
- Val-d’Or orogenic gold deposits formed by mixing of two fluids
- Supracrustal fluid: T < 280° C, δ¹⁸O < 2.8 ‰, δD > -10 ‰, ⁸⁷Sr/⁸⁶Sr(i) > 0.7022
- Deep-seated fluid: T > 490° C, δ¹⁸O > 9.3 ‰, δD < -40 ‰, ⁸⁷Sr/⁸⁶Sr(i) < 0.7007

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 δ¹⁸O 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 (⁸⁷Sr/⁸⁶Sr(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, form 0.701243 to 0.703641. A series of samples from the Sigma deposit displays no systematic variation with depth for δ¹⁸O values of quartz or tourmaline, δD values of tourmaline, temperature of equilibrium, or ⁸⁷Sr/⁸⁶Sr(i). The ⁸⁷Sr/⁸⁶Sr(i) of local komatiite, basalt, andesite, grauwacke and granodiorite, at 2.7 Ga, ranged from 0.681971 to 0.7128706. Country rocks with low ⁸⁷Sr/⁸⁶Sr(i) are likely a consequence of hydrothermal resetting of the Rb/Sr system in these samples.

Covariation of the calculated equilibrium δD_H2O and δ¹⁸O_H2O with quartz-tourmaline equilibrium temperatures indicates mixing between a low-δ¹⁸O (< 1.5 ‰), high δD (> -10 ‰), low temperature (< 280 °C) upper crustal fluid, and a high-δ¹⁸O (> 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 $\delta^{\text{D}}$ 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 $^{87}$Sr/$^{86}$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 (D1). 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 (D2) 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 (D₃) along the CLLTZ (Robert et al. 1995; Neumayr et al. 2000). D₂ 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 δ¹⁸O values, however, was shown for different deposits. The samples selected for this study are representative of the range in δ¹⁸O 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 BrF₅ according to the method of Clayton and Mayeda (1963) at the Stable Isotope Laboratory of Université Laval. The evolved CO₂ 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 δ¹⁸O 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 HNO₃ 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 HNO3, 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 (2σ).

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 HNO3 and Sr was separated from the matrix using a Sr-Spec resin. The purified Sr was dissolved in 5 ml of ~2% HNO3 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 ($^{84}\text{Kr}$), 86 ($^{86}\text{Kr}$) and 87 ($^{87}\text{Rb}$) were corrected by monitoring $^{83}\text{Kr}$ and $^{85}\text{Rb}$. The SRM987 standard was used to check external reproducibility, which on the long-term (90 measurements from April to September 2014) was 17 ppm (2σ: 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 $\delta^{18}$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 $\delta^{18}$O–$\delta^{18}$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 $\delta^{18}$O value of quartz, and the quartz-H$_2$O fractionation of Matsuhisa et al. (1979), the $\delta^{18}$O of water in equilibrium with quartz is estimated to have varied from 2.8 to 9.3 ‰ (Table 1).

The $\delta^{18}$O values of coexisting quartz and tourmaline are plotted in Figure 2B against the oxygen isotope fractionation between coexisting quartz and tourmaline ($\Delta_{Qz-Tur}$). Figure 2B shows that smaller $\Delta_{Qz-Tur}$ values are associated with higher tourmaline $\delta^{18}$O values, and that larger $\Delta_{Qz-Tur}$ values characterise tourmaline with lower $\delta^{18}$O values. The range in $\Delta_{Qz-Tur}$ values (1.8 ‰) is 3 times larger than the uncertainty of ±0.3 ‰ (Fig. 2B). Figure 2C is a plot of $\Delta_{Qz-Tur}$ values or the temperature of quartz-tourmaline oxygen isotope equilibrium, using Kotzer et al. (1993), versus the $\delta^{18}$O$_{H2O}$ computed from $\delta^{18}$O$_{Qz}$ and the fractionation of Matsuhisa et al. (1979), and from the $\delta^{18}$O$_{Tur}$ and the fractionation of Kotzer et al. (1993). Because of the difference in the calibration of the fractionations, the $\delta^{18}$O$_{H2O}$ 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-$\delta^{18}$O end-member, and a high-temperature, high-$\delta^{18}$O end-member (Fig. 2C). The T-$\delta^{18}$O$_{H2O}$ relation reflects the fact that the smaller $\Delta_{Qz-Tur}$ values, or higher temperatures, are associated with higher $\delta^{18}$O$_{Tur}$ values (Fig. 2B), or a heavier fluid in terms of oxygen isotope composition. Conversely, larger $\Delta_{Qz-Tur}$ values (or lower T) are associated with lower $\delta^{18}$O$_{Tur}$ 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 composition 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 $\delta^{18}$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 $\delta^{18}$O$_{tour}$ values and lower equilibrium temperature (Fig. 3).

Tourmaline $\delta$D 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 $\delta$D$_{H2O}$ values in equilibrium with tourmaline have a range from -34 to 29‰ (Table 1). The tourmaline $\delta$D and $\delta^{18}$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 $\delta$D of -34‰ and a higher $\delta^{18}$O of 7.6‰, and the second with a higher $\delta$D of 29‰ and a lower $\delta^{18}$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 $\delta$D$_{H2O}$ (-34 ‰) at high temperature, and higher $\delta$D$_{H2O}$ (19 ‰) at 400 °C (Fig. 4B). At temperatures lower than 400°C, the linear relation is broken and the $\delta$D 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 0.047x10^{-3} to 5.437x10^{-3}, with one value at 32.715x10^{-3}. The $^{87}$Sr/$^{86}$Sr ratios are from 0.701241 to 0.704409 (Table 1). The initial Sr isotope compositions ($^{87}$Sr/$^{86}$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 $^{87}$Sr/$^{86}$Sr$_{(i)}$ reported in Table 1. At the Sigma deposit, the six samples show no systematic variation in $^{87}$Sr/$^{86}$Sr$_{(i)}$ with depth (Fig. 3). The variation in $^{87}$Sr/$^{86}$Sr$_{(i)}$ correlates neither with 1/Sr (the highest 1/Sr has near average $^{87}$Sr/$^{86}$Sr$_{(i)}$; Fig. 6A), nor with Rb/Sr (Fig. 6B). The sample with the highest Rb/Sr has the lowest $^{87}$Sr/$^{86}$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 $^{87}$Sr/$^{86}$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 $^{87}$Sr/$^{86}$Sr ranging from 0.701243 to 0.703641, excluding one value at 0.709624. The $^{87}$Sr/$^{86}$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 ppm Rb (Table 2). Komatiitc rocks have up to 27 ppm Sr, and less than 3 ppm 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 $1/\text{Sr}$ (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 δ¹⁸O 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 δ¹⁸O values have a variance, at the deposit-scale, which is similar to the analytical precision (± 0.2 ‰). Quartz δ¹⁸O 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 δ¹⁸O 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 $\delta^{18}O_{Qz,Tur}$ 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 $\delta^{18}O$ values, or from 1.5 to 7.6 ‰ using tourmaline $\delta^{18}O$ values, and the quartz-tourmaline equilibrium temperature (Table 1). The difference in $\delta^{18}O_{H2O}$ 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 $\delta^{18}O$ values and using the assumption of isothermal conditions at 350 °C.

The covariation of $\delta^{18}O_{H2O}$ 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 $\delta^{18}O$ (Fig. 2B). Quartz and tourmaline yield similar values for $\delta^{18}O_{H2O}$ 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-$\delta^{18}O$ (< 1.5 ‰) fluid end-member had a lower temperature (<280 °C) than the high-$\delta^{18}O$ (>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 δ¹⁸O 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 δ¹⁸O 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 (δ¹⁸O = 5 ‰; δD = 0 ‰), and along a temperature gradient from 500º to 300ºC, yields a trajectory of δ¹⁸O 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 δ\(^{18}\)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 δ\(^{18}\)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 \(\times\) 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 δD\(_{\text{H}_2\text{O}}\) 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 δD\(_{\text{H}_2\text{O}}\) values is interpreted to record mixing between a high temperature (> 492 °C), low δD (<-40‰) 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 400ºC, the linear relation between δD_H2O and temperature is broken and δD_H2O 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 ºC, 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 ºC (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_H2O values below about 400 ºC (Fig. 4B).
The fact that $\delta_{\text{H}_2\text{O}}$ 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, $\delta_{\text{H}_2\text{O}}$ 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 $\delta_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values versus temperature are best explained by mixing of two main fluid end-member compositions. The low temperature (< 280°C), low $\delta^{18}\text{O}$ (< 1.5 ‰) and high $\delta$D (> -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, $\delta_{\text{H}_2\text{O}}$ values of the upper crustal fluid end-member. The high temperature (> 490 °C), high-$\delta^{18}\text{O}$ (> 9.3 ‰) and low $\delta$D (<-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 $^{87}$Sr/$^{86}$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 $^{87}$Sr/$^{86}$Sr(i) (Fig. 7B),
such that the range in $^{87}$Sr/$^{86}$Sr(i) is not a consequence of variation of the Rb content of

tourmaline. Instead, the tourmaline $^{87}$Sr/$^{86}$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 $^{87}$Sr/$^{86}$Sr(i) (0.70071 to 0.70225) must indicate that

the auriferous hydrothermal fluids had the same range in strontium isotope composition.

The $^{87}$Sr/$^{86}$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 δ$^{18}$O, high

temperature fluid end-member was characterized by higher $^{87}$Sr/$^{86}$Sr(i), whereas (ii) the

deep-seated, metamorphic, low δD, high δ$^{18}$O, high temperature fluid end-member had a
less radiogenic Sr isotope composition (Fig. 8). Lack of covariation between $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$, 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 $\delta D$ (>30 ‰), low $\delta^{18}\text{O}$ (<1.5 ‰) but radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (>0.7023), whereas the second end-member hydrothermal fluid had a higher temperature (>490 °C), low $\delta D$ (<-40 ‰), high $\delta^{18}\text{O}$ (<9.3 ‰) and non-radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (<0.7007).

5.3 Strontium sources

The Sr content and $^{87}\text{Sr}/^{86}\text{Sr}$ of the Val-d’Or area country rocks indicate that volcanic and plutonic rocks have low Sr (<2 to 295 ppm) and $^{87}\text{Sr}/^{86}\text{Sr}$ (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; Verpaelst 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; Verpaelst 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $\delta^{18}\text{O}$, 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‰), $\delta^{D}_{\text{fluid}}$ (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 $\delta^{D}$ 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 $\delta^{D}$ 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 $\delta^{18}$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 δ¹⁸O 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 $\delta^{18}O$ (2.8 to 9.3 ‰), $\delta D$ (-35 to 30‰), and $^{87}Sr/^{86}Sr_{(i)}$ (0.70071 to 0.70225). The covariation of $\delta D_{H2O}$ and $\delta^{18}O_{H2O}$ with temperature, and with $^{87}Sr/^{86}Sr_{(i)}$ of vein tourmaline indicates mixing between a low $\delta^{18}O$ (< 1.5 ‰), high $\delta D$ (> -10 ‰), high $^{87}Sr/^{86}Sr_{(i)}$ (> 0.7022), low temperature (< 280 °C) upper crustal fluid, and a high $\delta^{18}O$ (> 9.3 ‰), low $\delta D$ (< -40 ‰), low $^{87}Sr/^{86}Sr_{(i)}$ (< 0.7007), high temperature (> 490 °C) deep-seated metamorphic fluid. The high $\delta D$ 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 $^{87}Sr/^{86}Sr_{(i)}$ (<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 $^{87}$Sr/$^{86}$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 (Kerrich, 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.

7. Acknowledgements

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Voicu, G., Bardoux, M., Stevenson, R., Jebrak, M., 2000. Nd and Sr isotope study of hydrothermal scheelite and host rocks at Omai, Guiana Shield:
implications for ore fluid source and flow path during the formation of orogenic gold deposits. Mineralium Deposita, 35: 302 - 314.


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 $\delta^{18}$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 $\delta^{18}$O that is not in oxygen isotope equilibrium with quartz (Table 1). B) Plot of $\delta^{18}$O values for quartz and tourmaline versus the difference in composition $\Delta_{qz-tur}$. C) Plot of quartz-tourmaline oxygen isotope equilibrium temperature using Kotzer et al. (1993), versus the oxygen isotope composition of H$_2$O computed using quartz and tourmaline $\delta^{18}$O values (Table 1).

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

Figure 4. A) $\delta$D versus $\delta^{18}$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 $\delta$D$_{H_2O}$ 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 (Kerrich 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 (Kerrich 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.

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<td>Location</td>
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<td>Sample ID</td>
<td>Depth (m)</td>
<td>XRD Value</td>
<td>H2O δ18O (‰)</td>
<td>H2O δD (‰)</td>
<td>Sigma Deposits</td>
<td>Depth (feet)</td>
<td>Temperature (°C)</td>
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<td>96-DP-120</td>
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*: 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 $\delta^{18}$O$_{VSMOW}$ values in bold from Beaudoin et Pitre (2005). Equilibrium temperature using Kotzer et al. (1993). $H_2O \delta^{18}$O$_{VSMOW}$ and $\delta$D$_{VSMOW}$ 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.

<table>
<thead>
<tr>
<th>Rock</th>
<th>Sample</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Sr</th>
<th>Rb</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>$^{87}$Sr/$^{86}$Sr$_{(0)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bourlamaque Batholith (granodiorite)</td>
<td>YG-07-103</td>
<td>-77.5474</td>
<td>48.1446</td>
<td>185</td>
<td>43</td>
<td>0.726017</td>
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<td>YG-88-62</td>
<td>-77.6698</td>
<td>48.1589</td>
<td>227</td>
<td>44</td>
<td>0.722362</td>
<td>0.7004</td>
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<tr>
<td>Bevcon Pluton (granodiorite)</td>
<td>96-DP-65</td>
<td>-77.4375</td>
<td>48.0902</td>
<td>122</td>
<td>16</td>
<td>0.714642</td>
<td>0.6998</td>
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<td>YG-52-146</td>
<td>-77.4057</td>
<td>48.0938</td>
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<td>0.717128</td>
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<td>Sullivan Pluton (granodiorite)</td>
<td>YG-43-75</td>
<td>-77.6643</td>
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<td>198</td>
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<td>YG-35-59</td>
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<td>109</td>
<td>0.891088</td>
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<td>YG-71-35</td>
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<td>YG-82-47</td>
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<td>Komatiite</td>
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<td>Grauwacke</td>
<td>96-DP-05B</td>
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<td>0.727746</td>
<td>0.7014</td>
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</tbody>
</table>
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)

- Yilgarn (scheelite)
- Abitibi (scheelite)
- Abitibi (other minerals)
- Abitibi (tourmaline, previous studies)
- Val-d'Or (tourmaline, previous studies)
- Val-d'Or (tourmaline, this study)
- Val-d'Or (carbonates, QTC)
- Val-d'Or (carbonates, QC)
- Val-d'Or (grauwacke)
- Val-d'Or (granodiorite)
- Val-d'Or (volcanic)

**87Sr/86Sr(i)**

- Frequency

Open system alteration

BABI
Figure 6. Beaudoin & Chiaradia (2015)
Figure 7. Beaudoin & Chiaradia (2015)
Figure 8. Beaudoin & Chiaradia (2015)