Au-Bi-Te(-Cu) Mineralization in the Wawa Gold Corridor (Ontario, Canada): Implications for the Role of Bi-Rich Polymetallic Melts in Orogenic Au Systems

Elliot A. Wehrle 1,*, Iain M. Samson 1, Jean-François Montreuil 2 and Daniel J. Kontak 3

1 School of the Environment, University of Windsor, Windsor, ON N9B 3P4, Canada; ims@uwindsor.ca
2 Red Pine Exploration, Toronto, ON M5J 1H8, Canada; jfmontreuil@redpineexp.com
3 Harquail School of Earth Sciences, Sudbury, ON P3R 2C6, Canada; dkontak@laurentian.ca

* Correspondence: elliot.wehrle@sems-exploration.com

Abstract: The Wawa Gold Corridor, a series of Archean orogenic Au deposits in the Michipicoten greenstone belt, Canada, comprises two styles of Au mineralization: (1) syn-deformation gold associated with pyrite and arsenopyrite; and (2) late- to post-deformation gold associated with chalcopyrite and Bi-Te(-S) phases. Through petrographic and mineral–chemical analysis, it was determined that gold in the latter assemblages precipitated from Bi-rich polymetallic melts during hydrothermal overprinting of the earlier Au-As-S mineralization; this event was likely driven by the emplacement of Archean lamprophyres. The formation and evolution of these melts was governed by fluid–pyrite reaction interfaces, where the bulk composition of the melts was broadly controlled by the trace-element chemistry of the sulphide minerals in the local host rocks. This suggests that the melt-formation event involved mobilization of existing metal endowments related to early Au events, rather than addition of new Au, Bi, and Te. Thus, the deposition of high-grade Au by Bi-rich melts was dependent on pre-existing sulphide mineralization, both as a source of metals and as micro-environments that stabilized the melts. The paragenesis documented in the Wawa Gold Corridor (i.e., early hydrothermal Au-As-S mineralization and late melt-related Au-Bi-Te mineralization) has been previously recognized in numerous other orogenic and non-orogenic Au deposits. Herein, it is suggested that this apparent consistency in the timing of melt events across multiple systems probably reflects the physicochemical conditions (i.e., $f_{O_2}$-$a_{H_2S}$) of orogenic fluids being incompatible with molten Bi. Bi-rich polymetallic melts are hence unlikely to form primary Au mineralization in orogenic systems but can, however, have a significant impact on the ultimate deposit-scale distribution of Au via secondary mobilization and enrichment.

Keywords: gold transport; polymetallic melts; liquid Bi collector model; Archean orogenic gold deposits; sulphide trace-element analysis

1. Introduction

The ability of low-melting-point chalcophile-element (LMCE; e.g., Bi, Te, Ag, Pb) polymetallic melts to scavenge Au from hydrothermal fluids that are undersaturated with respect to gold [1,2] over ranges in temperatures similar to those typical of orogenic fluids (i.e., 200–400 °C; [3,4]) has led to the idea that polymetallic melts may play an important role in the formation of high-grade zones commonly encountered in orogenic Au deposits [2,5–7]. The association of Au with Bi and Te is also relevant to whether the progenitor Au-bearing hydrothermal fluids that form some orogenic deposits are of metamorphic and/or magmatic origin [8–12]. Given the apparent similarity in the isotopic and chemical nature of the fluids derived from these two reservoirs [3,8,13–15], the usefulness of the geochemical association of Au with various elements as evidence for a specific fluid source has been a subject of interest (see [16] and references therein), and mineral assemblages and compositions that reflect a Au-Bi-Te association are often
taken, in part, to be diagnostic of a magmatic–hydrothermal origin for ore metals [17–23]. Indeed, both the transport of Au in Bi-rich polymetallic melts and its association with Bi and Te have been repeatedly documented in a variety of magmatic–hydrothermal environments, including skarns [24–28], iron oxide copper–gold (IOCG) and iron oxide cobalt–gold–bismuth deposits [29,30], intrusion-related gold systems [31], greisens [32], and porphyry–epithermal systems [28,33,34]. However, despite the obvious relevance of Bi-rich polymetallic melts in orogenic deposits to discerning both the transport mechanism(s) for Au and potentially the source of Au-bearing fluids, only a few studies have investigated such processes in natural orogenic Au systems [7,17,21]. Although limited in number, these works collectively observed that melt-related Au-LMCE assemblages post-date orogenic Au + Fe-As-S mineralization at their respective deposits, which has been explained by the mobilization of Au and LMCEs out of orogenic sulphide minerals like pyrite [7,17] and/or by overprinting of existing orogenic mineralization by epithermal-style fluid events [17,21].

The present contribution explores the above issues by evaluating Au-Bi-Te(-Cu) assemblages in the orogenic Wawa Gold Corridor (WGC) in the Archean Michipicoten greenstone belt (MGB) of the Superior province, Canada. A previous study [35] determined that two principal Au events occurred in this system. The first is characterized by gold associated with arsenopyrite and pyrite hosted in quartz + carbonate + phyllosilicate schists and quartz veins, whereas the second is characterized by gold associated with Bi-Te minerals and chalcopyrite hosted in late, crosscutting, siderite–sulphide veinlets. The WGC therefore represents an excellent environment in which to investigate the nature and relevance of Bi-rich polymetallic melts in orogenic deposits and, as such, this study aims to assess: (1) whether or not Bi-rich melts existed and were responsible for depositing gold; (2) the physicochemical conditions under which any such melts originated and evolved; and (3) the relationship, if any, between Au-Bi-Te(-Cu) mineralization and magmatic–hydrothermal activity.

2. Geological Context

2.1. The Michipicoten Greenstone Belt and the Jubilee Stock

The WGC occurs in the Archean MGB in the Wawa subprovince of the Superior province (Figure 1a). The MGB is considered to be a continuation of the Au-endowed Abitibi greenstone belt [36–38] and is a Au district that has attracted significant interest in recent years due to the presence of several active mines and exploration camps (Figure 1a). A number of these have been the focus of research activities, including the WGC [35,39], the Island Gold deposit [40–42], the Magino deposit [43], and the Missanabie–Renabie deposit [44–47].
Figure 1. (a) Regional geology of the Michipicoten greenstone belt, modified after data from the Ontario Geological Survey MRD 126-1 [48]; deposit locations are from the Mineral Deposit Inventory of Ontario (https://data.ontario.ca/dataset/mineral-deposit-inventory-of-ontario, accessed on 18 August 2023). The red box over the outline of Ontario in (a) indicates the location of the geological map in (a). (b) Simplified geology of the Jubilee Stock, modified after Red Pine Exploration’s internal maps.
The MGB was formed from three periods of bimodal volcanism and related intermediate to felsic plutonism, each separated by intervals of sedimentation [49], at 2890 Ma, 2750 Ma, and 2700 Ma [50]. Like the other shear-zone-hosted Au deposits in the MGB [40–45], the WGC is spatially associated with plutonic rocks, in this case the Jubilee Stock (Figure 1b). This 2745 Ma intrusion [51] is dominated by amphibole–biotite diorite and tonalite (Figure 2a), with some temporally equivalent volcaniclastic rocks (Figure 2b). It is cut by a suite of mafic dikes which pre-date regional deformation (Figure 2c), by the younger (ca. 2450) Matachewan dike swarm [39,52], as well as by two sets of lamprophyre dikes. The older Archean lamprophyre dikes (2700–2670 Ma; [53,54]) in the WGC may be weakly deformed, pervasively carbonatized, and are associated with a pink alteration assemblage comprising K-feldspar and carbonate (Figure 2d). Such alteration is often intense and can locally result in pervasive replacement of the host schists, imparting a characteristic pink-red colour (Figure 2e vs. Figure 2f). The younger Proterozoic lamprophyre dikes, associated with the emplacement of the 1.0 Ga Firesand River carbonatite complex (location marked in Figure 1a; [55,56]), are relatively undeformed, cut existing structural fabrics, and are associated with a greenish-blue alteration assemblage comprising mainly calcite and riebeckite (Figure 2g).

Figure 2. Rock types of the Jubilee Stock: (a) coarse-grained, least-deformed amphibole diorite; (b) quartz + plagioclase porphyritic unit; (c) deformed mafic dike with marginal quartz veins cutting least-deformed tonalite; (d) Archean lamprophyre dike with pink K-feldspar + siderite alteration halo; (e) quartz–carbonate–sericite schist, relatively unaffected by K-feldspar + siderite alteration; (f) schist with pervasive K-feldspar + siderite alteration (note the pink-red colour); and (g) Neoproterozoic lamprophyre dikes with blue-green riebeckite + calcite alteration haloes; Abbreviations: Qz = quartz; Rbk = riebeckite; Cal = calcite; Kfs = K-feldspar; and Sd = siderite.
2.2. Structural and Hydrothermal Evolution of the Wawa Gold Corridor

The detailed structural and mineralogical history of the WGC is documented in Wehrle et al. [35] and is summarized below. The Jubilee Stock was affected by pre-deformation hydrothermal alteration (D₀), which comprised the destruction of igneous feldspar and formation of hydrothermal albite, quartz, biotite, chlorite, and sericite. Gold mineralization is hosted by several shear zones that formed during three periods of brittle–ductile deformation (D₁–D₃). Most of the mineralization initially formed as Au dissolved in arsenopyrite (Apy₁) during syn-D₁ fluid flow. Various sulphide replacement reactions subsequently destroyed much of this arsenopyrite and formed disseminated gold with associated sulphides (dominantly pyrite, pyrrhotite, and relic arsenopyrite). These gold + sulphide assemblages, which occur in quartz + phyllosilicate + carbonate schists and veins in NW- and NE-striking D₁–D₂ structures, define the first style of Au mineralization in the WGC (Figure 3a–d). The Jubilee Shear Zone (JSZ), the largest Au-bearing structure on the property (indicated resource of 205,000 oz Au at an average grade of 5.31 g/t Au and cut-off of 2.7 g/t Au, inferred resource of 396,000 oz Au at an average grade of 5.22 g/t and cut-off of 2.7 g/t Au; https://redpineexp.com/projects/wawa-gold-project/, accessed on 18 August 2023), is mainly characterized by D₂ deformation features (e.g., shallowly southward-plunging L₂ and NNE- and NE-striking, moderately dipping S₂) and is dominated by this style of Au mineralization. D₃ deformation formed NNW-striking shear zones (<10 m in width), a salient feature of which are decimetre- to metre-scale tourmaline-bearing shear and extension veins (Figure 3e). These D₃ veins are also present in the earlier structures, such as the JSZ, where they overprint pre-existing fabrics (S₁ and S₂), and in the least-deformed Jubilee Stock. Regardless of their structural character (i.e., shear vs. extension) and environment of formation (i.e., the various shear zones or the least-deformed Jubilee Stock), the D₃ veins comprise quartz + tourmaline + carbonate + pyrite ± chlorite ± pyrrhotite ± chalcopyrite and typically contain seams or laminae of tourmaline and/or chlorite. The Minto Shear Zone (MSZ) hosts the largest concentration of gold currently known in a D₃ structure (Figure 1b) in the Minto Mine South deposit and the former Minto Mine (indicated resource of 25,000 oz Au at an average grade of 7.5 g/t Au and cut-off of 3.5 g/t Au, inferred resource of 75,000 oz Au at an average grade of 6.6 g/t and cut-off of 3.5 g/t Au, and 23,152 oz Au of former production in the Minto Mine; https://redpineexp.com/projects/wawa-gold-project/, accessed on 18 August 2023). The D₃ veins are themselves crosscut by carbonate-rich assemblages that host the second style of Au mineralization in the WGC, this being gold with Bi-Te phases and chalcopyrite (Figure 3f), with such assemblages being the focus of this study. Based on available age constraints on deformation elsewhere in the MGB [41,42,47], the D₁–D₃ events noted above likely occurred between 2720 and 2672 Ma.

The sulphide mineralogy of the WGC, which is described and discussed in Wehrle et al. [35], mainly comprises: (1) pre-deformation pyrite (Py₀), arsenopyrite (Apy₀), and pyrrhotite, which occur disseminated through least-deformed rocks of the Jubilee Stock, such as in the footwall of the JSZ; (2) syn-D₁ arsenopyrite (Apy₁), pyrite (Py₁A-B), and pyrrhotite, which are locally disseminated within the JSZ and in smaller D₁ structures that cut the stock; (3) syn-D₂ pyrite (Py₂A-B), which is the dominant sulphide phase in the JSZ, with accessory pyrrhotite; (4) syn-D₃ pyrite (Py₃A-B) and pyrrhotite, which occur in the D₃ veins; and (5) late pyrite (Py₄) and chalcopyrite, which occur in the carbonate veinlets that cut the D₃ veins.
Figure 3. Styles of gold mineralization in the WGC: (a,b) D1 chlorite + muscovite + quartz + carbonate schist with bands of fine-grained disseminated arsenopyrite that host gold; (c,d) D2 quartz + muscovite + carbonate schist hosting porphyroblastic Py2 with inclusions of gold; (e,f) D3 quartz + tourmaline + carbonate vein with late carbonate-rich assemblages that host gold with chalcopyrite and Bi-Te minerals (in this case, tsumoite). (b,d,f) are reflected-light photomicrographs. Additional abbreviations: Au = gold; Apy = arsenopyrite; Py = pyrite; Cb = carbonate; Chl = chlorite; Ms = muscovite; Sd = siderite; Ccp = chalcopyrite; Tsm = tsumoite (BiTe).

3. Methods

3.1. Petrography and Mineral Identification

Numerous Au-Bi-Te occurrences have been documented throughout the Jubilee Stock by mapping, trenching, and drilling activities (cf. Figure 1b). The samples investigated in the current study are a subset of a larger suite that was collected to investigate Au mineralization in the JSZ, the MSZ, and the networks of extensional veins and shear-hosted veins in the Jubilee Stock (cf. Figure 1b, [35]). The samples studied in detail include: (1) three Au-Bi(-Te)-rich samples from a set of extensional D3 veins located in the footwall of the JSZ (Location 1, Figure 1b); and (2) seven Au-Bi(-Te)-rich samples from D3 veins within and adjacent to the MSZ (Location 2, Figure 1b). Petrographic analysis involved both transmitted- and reflected-light microscopy of polished thin sections using
an Olympus BX-51 microscope, and scanning-electron microscope back-scattered electron (SEM-BSE) imaging. Mineral compositions were determined with SEM energy-dispersive X-ray spectroscopy (EDS) on an FEI Quanta 200 FEG environmental SEM fitted with an EDAX EDS detector at the University of Windsor (Windsor, ON, Canada). The operating conditions included an acceleration voltage of 20.0 kV, an integration time of 30 s, and a spot size of 4 µm.

3.2. Sulphide Trace-Element Chemistry

The trace-element chemistry of pyrite and arsenopyrite was determined using laser-ablation inductively-coupled plasma mass-spectrometry (LA-ICP-MS) housed at the University of Windsor. The following isotopes were measured: \( ^{34}S, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{82}Se, ^{95}Mo, ^{107}Ag, ^{109}Ag, ^{121}Sb, ^{130}Te, ^{184}W, ^{197}Au, ^{208}Pb, \) and \(^{209}Bi\). Several isotopes were also measured to monitor contamination from adjacent gangue minerals, these being \( ^{27}Al, ^{29}Si, ^{44}Ca, \) and \(^{48}Ti\). Transects across individual mineral grains were performed with a PhotonMachines 193 nm nanosecond Ar-F Analyte Excite excimer laser coupled to an Agilent 7900 quadrupole mass spectrometer using a laser energy of 4.1 µJ and a pulse rate of 20 Hz. The beam size was 25 µm and the transect speed was 5 µm/s.

4. Results

4.1. Mineral Paragenesis and Petrography of D\(_3\) Veins

The D\(_3\) veins in the MSZ and the footwall of the JSZ dominantly comprise granoblastic, polygonal quartz, isolated patches of coarse-grained calcite, and laminations composed of fine-grained tourmaline and chlorite (cf. Figures 3e and 4a). Sulphide minerals (<5 modal %) typically occur in contact with seams of tourmaline or inclusions of wall rock. Pyrrhotite, the most abundant sulphide phase in these samples, is present as anhedral aggregates up to a few centimetres across. Pyrrhotite rarely envelopes euhedral pyrite (Py\(_3A\)); in such cases, the grain boundaries between these two minerals are typically planar (Figure 4b). Aggregates of pyrrhotite are usually mantled and veined by anhedral pyrite (Py\(_3B\); Figure 4c), which is the dominant textural variety of pyrite in most of the D\(_3\) veins. Siderite veinlets crosscut the D\(_3\) veins (Figure 4d) and in places contain accessory K-feldspar (Figure 4e) or chalcopyrite (Figure 4f). The siderite is sometimes surrounded by interstitial calcite (Figure 4g) and replaced by riebeckite (Figure 4h). The siderite veinlets also form alteration rims around blebs of pyrrhotite + Py\(_3B\), with Py\(_3B\) partially replaced by siderite and chalcopyrite (Figure 4i). A later stage of fine-grained, euhedral pyrite (Py\(_4\)) is hosted by the siderite that replaced Py\(_3B\); notably, this pyrite generation occurs along the margins of the siderite (Figure 4j). It is these siderite + chalcopyrite + Py\(_4\) assemblages that are the main host for Bi-Te phases (Figure 4k) and gold (Figure 4l) in the D\(_3\) veins. Gold occurs as individual grains hosted by various gangue minerals (Figure 5a–d), in association with chalcopyrite (Figure 5e,f), or with chalcopyrite and Bi-Te phases (Figures 3f, 6, and 7).

Based on the above microscopic observations and further macroscopic observations of D\(_3\) veins throughout the WGC and Jubilee Stock, the paragenesis of D\(_3\) veins can be divided into three principal stages: (1) syn-deformation (D\(_3\)) quartz, tourmaline, calcite, Py\(_3A\), pyrrhotite, and Py\(_3B\); (2) late- to post-D\(_3\) siderite (i.e., as alteration rims on Py\(_3B\) and as veinlets), K-feldspar, chalcopyrite, Py\(_4\), Bi-Te minerals, and gold; and (3) post-D\(_3\) riebeckite and calcite.
Figure 4. Mineral assemblages and textures in D3 veins: (a) coarse calcite and tourmaline with quartz; (b) sharp contacts between euhedral Py3A and surrounding anhedral pyrrhotite; (c) infiltration and replacement of pyrrhotite by anhedral Py3B; (d) siderite veinlets cutting D3 vein quartz; (e) siderite + K-feldspar veinlets cutting D3 vein quartz; (f) siderite + chalcopyrite veinlets cutting D3 vein quartz; (g) calcite after siderite in a veinlet that cuts D3 vein quartz; (h) replacement of siderite by riebeckite; (i) replacement of Py3B by chalcopyrite and siderite; (j) localisation of euhedral Py4 in the exterior margins of the siderite alteration envelope around Py3B (note the planar contacts between Py4 and siderite); (k) tsumoite in the siderite alteration halo around a bleb of pyrrhotite and Py3B; and (l) gold in the siderite alteration halo around a bleb of pyrrhotite and Py3B. (a) is a transmitted-light photomicrograph, (d) is a cross-polar photomicrograph, (b,c,f,i–l) are reflected-light photomicrographs, and (e,g,h) are BSE images. The dashed white line in (i) approximates the boundary between the siderite alteration rim and the D3 vein quartz. Additional abbreviations: Po = pyrrhotite; Tur = tourmaline.
4.2. Petrography and Composition of Au-Bi-Te-Bearing Mineral Assemblages

Assemblages of Au ± Bi ± Te minerals are present either in siderite-rich alteration rims around Py3B, along with chalcopyrite and in some cases Py4, or along fractures in quartz adjacent to Py3B. Two basic groups of assemblages are distinguished based on mineral composition and location (Table 1 and Table S1). The first group occurs in the D3 vein samples from the footwall of the JSZ (“F-JSZ assemblages”; Location 1 in Figure 1b) and is dominated by gold and tsumoite (BiTe). The second group occurs in D3 veins that are located in and adjacent to the MSZ (“MSZ assemblages”; Location 2 in Figure 1b), and is dominated by gold, bismuth, and maldonite, but also contains a variety of accessory phases. The F-JSZ assemblages are relatively Te-rich and almost entirely composed of tsumoite (BiTe) and gold, which share curvilinear boundaries (Figure 6a) and meet at ~120° triple junctions with chalcopyrite (Figure 6b,c). Tsumoite is also observed as anhedral grains that co-exist with Py4 and siderite (Figure 6d). In some places, tetradymite (≈Bi2Te2S) occurs around tsumoite; the boundaries between these phases are irregular (Figure 6e). The F-JSZ assemblages have bulk compositions of approximately Bi ≈ Te > Au (as inferred from the abundance of tsumoite relative to gold).

Figure 5. Occurrence of gold in D3 veins without Bi-Te minerals: (a,b) gold hosted by a riebeckite + calcite corona around Py3B; (c,d) gold hosted by a siderite + Py4 alteration zone around Py3B; and (e,f) gold associated with chalcopyrite and Py4 in a siderite veinlet cutting D3 shear vein quartz. All images are reflected-light photomicrographs. The coloured boxes in (a,c,e) outline the locations of (b,d,f), respectively.
Table 1. Compositions and formulae of the Au-Bi-Te(-S-Se) minerals, as measured by EDS.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Occurrence</th>
<th>Formula</th>
<th>( n )</th>
<th>Element Concentration (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Au</td>
<td>Ag</td>
<td>Bi</td>
</tr>
<tr>
<td>Gold</td>
<td>F-JSZ and MSZ assemblages</td>
<td>Au</td>
<td>17</td>
<td>97</td>
</tr>
<tr>
<td>Bismuth</td>
<td></td>
<td>Bi</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Maldonite</td>
<td></td>
<td>Au2Bi</td>
<td>12</td>
<td>72</td>
</tr>
<tr>
<td>Bismuthinite</td>
<td>MSZ assemblages</td>
<td>Bi7S5</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>Jonassonite</td>
<td></td>
<td>AuBi5S4</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>Parkerite</td>
<td></td>
<td>Ni3Bi2S2</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Tsumoite</td>
<td>F-JSZ and MSZ assemblages</td>
<td>BiTe</td>
<td>11</td>
<td>48</td>
</tr>
<tr>
<td>Tetradymite</td>
<td>F-JSZ assemblages</td>
<td>Bi2Te2S</td>
<td>13</td>
<td>36</td>
</tr>
</tbody>
</table>

All element concentrations are in atomic percent. All values are averages. \( n \) = number of analyses. Average absolute uncertainty (±) for each element is given in atomic percent, as determined by averaging the products of percentage error and atomic percent for each measurement.

In contrast to the F-JSZ assemblages, MSZ assemblages are Bi-rich and mostly comprise gold, maldonite (Au2Bi), and bismuth, with trace occurrences of jonassonite (AuBi5S4; Figure 7a), tsumoite (Figure 7b), ingodite (Bi(Te0.55S0.36Se0.09)), parkerite (Ni3Bi2S2), and bismuthinite (Bi2S3). Intergrowths of gold and bismuth are present (Figure 7c), as are trails of globular grains of gold, maldonite, and bismuth along healed fractures in vein quartz (Figure 7d,f). Where bismuthinite is present, it generally envelops bismuth and gold (Figure 7e) or occupies fractures and grain boundaries in vein quartz (Figure 7f).
Unlike the F-JSZ assemblages, these assemblages do not share contacts with Py\textsubscript{4}. The bulk composition of the MSZ assemblages is Bi > Au >> Te. The paragenetic relationships of the D\textsubscript{3} veins and late/post-D\textsubscript{3} assemblages that cut these veins, in relation to the evolution of the WGC, are presented in Figure 8.

Figure 7. Textural relationships amongst MSZ assemblages: (a) curvilinear boundaries between bismuth and jonassonite, as well as the occurrence of blebs of bismuth and maldonite within chalcopyrite (note the planar contacts between siderite and jonassonite and siderite and maldonite); (b) blebs of tsumoite disseminated throughout siderite without Py\textsubscript{4}; (c) intergrowths of gold and bismuth adjacent to chalcopyrite; (d) trails of spherical grains of gold, maldonite, and bismuth along fractures in shear vein quartz; (e) bismuthinite forming around gold and bismuth; and (f) trails of bismuth blebs in vein quartz and bismuthinite emplaced along grain boundaries in vein quartz. All are BSE images. Additional abbreviations: Bi = bismuth; Mld = maldonite; Jon = jonassonite; Bsm = bismuthinite.

4.3. Mineral Chemistry

The complete trace-element dataset for the WGC sulphides is presented in Wehrle et al. [35] and data for Au, Ni, Bi, and Te are summarized in Figure 9a. The key points for this contribution are as follows: (1) the concentrations of Au, Bi, and Te in Py\textsubscript{3B} and Py\textsubscript{4} are comparable, although Au is overall higher in Py\textsubscript{3B}; (2) Te concentrations are similar in most generations of pyrite and arsenopyrite, but Bi concentrations are notably lower in Py\textsubscript{0} and ApPy\textsubscript{0}; and (3) the concentrations of Ni in ApPy\textsubscript{0} and Py\textsubscript{0} are somewhat lower than those of the other generations of pyrite and arsenopyrite, whereas Py\textsubscript{3B} is enriched in Ni. The differences in Bi and Te concentration amongst these sulphides are highlighted by plotting Ni against Te/(Bi + Te) (Figure 9b), which emphasizes the comparatively Te-rich, Bi-poor nature of ApPy\textsubscript{0} and Py\textsubscript{0} compared to the other sulphides. This latter observation is pertinent, as these sulphides are more abundant in the footwall of the JSZ, where the F-JSZ assemblages were documented, as compared to the MSZ (which is richer in Py\textsubscript{3A-B}).
4.3. Mineral Chemistry

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**Figure 8.** Hydrothermal mineral paragenesis for the WGC. The strike–dip symbols represent the dominant orientation of the foliations in the shear zones formed during each deformation event, and the red arrow denotes a stretching lineation. The relative thickness of the lines corresponds to the relative abundance of the mineral phases. Additional abbreviations: Ab = albite; Bt = biotite; Gn = galena; Mol = molybdenite; Pke = parkerite.
pertinent, as these sulphides are more abundant in the footwall of the JSZ, where the F-JSZ assemblages were documented, as compared to the MSZ (which is richer in Py₃A-B).

Figure 9. Trace-element characteristics of the dominant sulphide generations in the WGC. Note the relatively lower concentrations of Bi in Apy₀ and Py₀ (the most abundant sulphides in the footwall of the JSZ) as compared to the other sulphide generations, as well as the comparable concentrations of Au, Bi, and Te between Py₃B and Py₄ (a). The bivariate plot in (b) demonstrates that the sulphides in the footwall of the JSZ tend to have greater proportions of Te (as compared to Bi) and lower concentrations of Ni than those in the MSZ.

5. Discussion

5.1. Melt vs. Hydrothermal Assemblages in Late Veinlets

The mineralogy and textures of most of the assemblages that cut D₃ veins (siderite, K-feldspar, calcite, riebeckite, chlorite, and Py₄) are consistent with a hydrothermal origin. These assemblages also contain LMCE-bearing phases (chalcopyrite and minerals that belong to the MSZ and F-JSZ assemblages); however, assessing whether some or all LMCE-bearing phases precipitated from hydrothermal fluids or from melts requires careful textural analysis [25,57,58]. Chalcopyrite largely occurs as anhedral patches that overprint Py₃B (Figure 4i,j); these textures are consistent with the hydrothermal replacement of the latter by the former. Although textural evidence exists for the co-crystallization of chalcopyrite with other LMCE phases (e.g., 120° triple junctions with tsumoite and gold;
Figure 6c), this does not discount the possibility that chalcopyrite was hydrothermal (as the precipitation of solid phases from the hydrothermal fluids and polymetallic melts could have been contemporaneous). Furthermore, chalcopyrite is significantly more abundant than the associated Au-Bi-Te minerals, which, if chalcopyrite also crystallized from a melt, would have required melts dominated by Cu. This is unreasonable, however, given the high melting point of Cu-rich melts. For example, in the Cu-Bi binary system, a melt composition of 50% Cu requires temperatures in excess of 800 °C [59]. As with chalcopyrite, gold occurs both in direct association with Au-Bi-Te phases and in the absence of these phases. Grains of gold belonging to the latter category have anhedral morphologies (Figure 5a–f) and, given the lack of spatial proximity to LMCE assemblages, probably did not form from melts.

In contrast to the above, minerals belonging to F-JSZ assemblages (tsunoite, gold, and tetradymite) display mutual curvilinear boundaries (Figure 6a), a feature consistent with equilibrium crystallization from a melt [58]. Some MSZ assemblages contain intergrowths of bismuth and gold (Figure 7c), a texture similar to those produced during Bi-Au melting experiments [6] and observed in natural environments where melting has been invoked as the mechanism for Au-Bi transport [18,25]. Globular blebs of bismuth, maldonite, and gold that are aligned along fractures in vein quartz of the MSZ (Figure 7d) provide compelling evidence for transport in molten form, as their spherical morphologies are consistent with the immiscibility of the polymetallic melts in a coexisting hydrothermal fluid [23,32], the latter being required for precipitation of the carbonates, silicates, chalcopyrite, and pyrite (Py₄) that occur with, and in some cases enclose, the Au-Bi-Te assemblages. In light of these textural relationships, both the F-JSZ and MSZ LMCE assemblages are interpreted to have formed from polymetallic melts. These assemblages will be the focus of the remaining discussion.

5.2. Sources of Au, Bi, and Te

In order to develop a complete model for the WGC mineralization, the source(s) of the Au, Bi, and Te that occur in the late-stage assemblages described above needs to be addressed. Based on the paragenesis established herein, in which the MSZ and F-JSZ assemblages occur in and proximal to siderite-rich assemblages that replace Py₃B, it could be posited that these elements were sourced from Py₃B, where: (1) Py₃B crystallized during the formation of quartz + tourmaline + carbonate veins; (2) carbonic hydrothermal fluids dissolved Py₃B, thereby liberating Au, Bi, and Te, and precipitated siderite; and (3) the aforementioned elements were mobilized on a local (i.e., centimetre) scale in the form of Bi-rich polymetallic melts to form the now observed Bi-Te-Au-S bearing phases, bismuth, and gold. Analogous models for the liberation of Au and other metals from paragenetically early pyrite (or arsenopyrite) have been proposed for other systems, in which hydrothermal alteration [7,21,60–62] or metamorphism [63,64] were invoked as mechanisms for the reconstitution of Au-bearing sulphides or sulfarsenides and the related expulsion of trace metals. Some of these studies linked such processes to the generation of Bi-Te-rich polymetallic melts [7,21,65].

A mass–balance analysis was employed to assess whether the dissolution of Py₃B could have locally (cm scale) sourced the Au, Bi, and Te that constitute the melt assemblages in the D₃ veins. This was conducted by comparing the mass of an element released during Py₃B dissolution with the total mass of that element in a given assay interval (approximately one metre of halved HQ drill core):

\[
%E_{Py3B} = \left( \frac{C_{Py3B} \times V_{sid} \times D_{py}}{C_{WR} \times V_{WR} \times D_{WR}} \right) \times 100\%
\] (1)

In Equation (1), %E is the percent contribution from Py₃B of an element by mass, C is the concentration of an element in ppm in Py₃B or whole rock (WR), Vsid is the modal volume of siderite as a percentage of the assay interval, and D is the density of the material (pyrite or whole rock). It is assumed that the replacement of Py₃B by siderite was a constant-volume process, as supported by textural observations (cf. Figure 4i–k). The average of
C_{Py3B} over a given assay interval was used with a range of values in V_{sid} to assess the amount of Py_{3B} dissolution required to account for whole-rock enrichment in each element. This calculation (Figure 10) indicates that unreasonably large amounts of Py_{3B} would have been required to provide the necessary concentrations of Au, Bi, and Te. Even if D_{3} veins were originally 50% Py_{3B} by volume, the loss of pyrite could account for the mass of Au, Bi, and Te that is present only in low-grade samples, but not in higher-grade samples. In addition, if such high initial volumes of Py_{3B} were present, it would be expected that relics of massive sulphide would be preserved in some veins, which is not the case. In fact, petrographic observations suggest that no more than 1–2 modal % of the Py_{3B} was lost during its replacement by siderite. This means that pyrite dissolution (i.e., Py_{3B}) likely accounted for no more than one percent of the masses of Au, Bi, and Te in the D_{3} veins (blue dots in Figure 10). Thus, a model in which Bi-rich polymetallic melts formed adjacent to pyrite grains as a result of the liberation of trace metals during the replacement of Py_{3B} is not valid for the D_{3} vein systems in the WGC.

Figure 10. Results of mass–balance calculations performed to assess the potential of Py_{3B} to have been the source of the Au, Bi, and Te found in the D_{3} veins. The percentage is that of the contribution of each element by mass from Py_{3B} (as outlined in Equation (1) in the text) against the whole-rock concentration of the element. Each point represents an individual sample from which multiple grains of Py_{3B} (n = 5–10) were analysed using LA-ICP-MS to determine an average concentration of Au, Bi, and Te in Py_{3B}. The coloured series represent the percentage of each element by mass that could have been generated assuming theoretical starting modal volumes of Py_{3B} (and if all of this pyrite was dissolved). Note that based on drill core and petrographic observations, the 1% series (blue points) is the most accurate.

The preceding analysis means that significant amounts of Au, Bi, and Te were already present in the hydrothermal fluids that transgressed the D_{3} veins when Py_{3B} was dissolved, such that the origin of these fluids requires further evaluation. Two observations are
pertinent to this evaluation. First, the Au-Bi-Te assemblages are consistently located in
D₃ veins (and not in D₁–D₂ veins, schists, and least-deformed host rocks elsewhere in the
WGC), which suggests that D₃ structures played a key role in focusing the fluids responsible
for the late Au-Bi-Te melt event. Second, the siderite ± chalcopyrite ± K-feldspar veinlets
that cut D₃ veins (cf. Figure 4e) and that host Au-Bi-Te assemblages on the margins of
Py₃₉ are conspicuously similar in composition to the Fe-carbonate + K-feldspar alteration
assemblages known to be associated with the Archean lamprophyres throughout the
deposit (cf. Figure 2d,f).

Based on this, it is posited that the hydrothermal fluid + melt event that formed
the Au-Bi-Te assemblages was related to the emplacement of the Archean lamprophyres
and that this occurred during the later stages of D₃. This model explains the spatial
relationship between the Au-Bi-Te assemblages and D₃ veins and is compatible with the age
of the Archean lamprophyres (2700–2670 Ma) as compared to the available age constraints
previously noted for regional deformation in the MGB (2720–2672 Ma). Importantly, the
model describes a fluid event that: (1) post-dates orogenic As-Au-S mineralization (i.e.,
D₁ and D₂ arsenopyrite/pyrite + Au; [35]); and (2) was contemporaneous with magmatic
activity (i.e., the emplacement of the Archean lamprophyres).

Lamprophyric magmas have previously been considered as a plausible source of Au
in orogenic systems due to their spatial association with some orogenic Au deposits [66,67].
In light of a large body of geochemical data, however, this model was largely discarded
and the co-occurrence of lamprophyre dikes with orogenic deposits was instead related
to the exploitation of similar crustal structures by both hydrothermal fluids and lampro-
phyric magmas [68–72]. In the WGC, as described above, the alteration linking the melt
assemblages and dikes, and their timing, indicate that Archean lamprophyre dikes may
have introduced substantial quantities of Au, Bi, or Te to the system. However, as the dikes
are ubiquitous throughout the Jubilee Stock but the late-stage Au-Bi-Te mineralization
only occurs in D₃ veins where the dikes cut previously mineralized structures, it is more
likely that the hydrothermal fluids associated with the melt event caused mobilization of
pre-existing metal enrichment (i.e., in D₀–D₃ sulphides). This model requires deposit-scale
transfer of these elements, as the source sulphide minerals (D₀–D₃ arsenopyrite and pyrite)
 occur throughout the least-deformed host rocks and shear zones of the WGC, whereas the
melt assemblages occur only in the D₃ veins.

5.3. Compositional Differences between MSZ and F-JSZ Assemblages

Based on the existing geological and petrographic data discussed above, we have
concluded that the Au, Bi, and Te that occur in the MSZ and F-JSZ assemblages were
scavenged from the various earlier generations of arsenopyrite and pyrite by hydrothermal
fluids contemporaneous with the emplacement of Archean lamprophyres during the later
stages of D₃. However, these two groups of assemblages are distinct in terms of their
mineralogy: F-JSZ assemblages are dominated by tsumoite and gold, with rare tetradymite,
whereas MSZ assemblages are dominated by bismuth, gold, and maldonite, with minor
jonassonite, tsumoite, ingodite, parkerite, and bismuthinite. In both groups, the latest phase
is a relatively S-rich mineral that post-dates relatively S-poor minerals (e.g., tetradymite
after tsumoite and bismuthinite after bismuth; Figures 6e and 7e, respectively). These
differences in mineralogy correspond to differences in bulk composition: F-JSZ assemblages
have Bi ≈ Te > Au and MSZ assemblages have Bi > Au >> Te. The MSZ assemblages are also
S-rich compared to the F-JSZ assemblages (as inferred from the rare presence of jonassonite
and ingodite). These compositional differences could exist for a variety of reasons.

The first possible reason is that the two assemblages represent temporally distinct
mineralizing events. This seems unlikely given their overall similarities in paragenesis with
respect to the characteristics of D₃ veins in the WGC; both MSZ and F-JSZ assemblages
occur with chalcopyrite on the margins of pyrite + pyrrhotite aggregates in carbonate
veinlets that crosscut D₃ veins.
The second consideration is spatial, where the assemblages reflect differences in the geochemistry of the parts of the system that host the two assemblages. Assuming that, prior to melt mobilization, most of the Bi and Te was hosted in sulphides (e.g., pyrite, arsenopyrite), the composition of these minerals provides a reasonable proxy for the availability of Bi and Te in each environment. It is therefore noteworthy that the dominant sulphides in the footwall of the JSZ (Py0, Apy0), which are the sulphides in greatest proximity to the F-JSZ assemblages studied, are richer in Te and substantially poorer in Bi than those in the MSZ (Py3A-Bi; cf. Figure 9b). This is consistent with the differences in the two assemblages in a model where the hydrothermal fluids that co-existed with the polymetallic melts were responsible for the redistribution of Au, Bi, and Te within the deposit, rather than the introduction of these elements to the deposit. The chemistry of D0–D3 pyrite and arsenopyrite that originally sequestered these elements thus influenced the compositions of the polymetallic melts that formed in the two locations (MSZ and footwall of the JSZ).

The final considerations are physicochemical in nature, as numerous studies have demonstrated that parameters like fO2, fTe2, and aH2S impact the proportions of Bi relative to Te, S, and Se in minerals containing these elements [5,18,33,73]. More specifically, minerals with Bi ≤ (Te + Se + S) form under relatively high fO2-aH2S conditions (pyrite-stable), whereas those with Bi ≥ (Te + Se + S) form under relatively low fO2-aH2S conditions (pyrrhotite-stable). Tsumoite (BiTe) may form under either pyrite- or pyrrhotite-stable conditions [5]. The F-JSZ assemblages (e.g., tsumoite and the tetradymite; BiTe and Bi2TeS3, respectively) have stoichiometries with Bi ≤ (Te + Se + S), whereas MSZ assemblages (e.g., bismuth, maldonite, jonassonite, ingodite, parkerite; Bi, Au2Bi, AuBi5S4, Bi2TeS, and Ni3Bi2S2, respectively) have stoichiometries with Bi ≥ (Te + Se + S) (Figure 11). The only exception in the MSZ assemblages is bismuthinite (Bi2S3), which post-dates the other MSZ assemblage minerals. It could therefore be posited that these different bulk compositions reflect different fO2-aH2S conditions in the two environments. However, the consistency in the composition of the gangue minerals in the two environments (dominantly siderite, Py4, and chalcopyrite) does not point to significant differences in these parameters. It remains possible that the differences in fO2 and aH2S between the footwall of the JSZ and the MSZ were large enough to impact the stability of the LMCE-bearing phases without affecting the stability of the gangue phases, but additional data would be required to test this (e.g., fluid inclusion studies). Conversely, it is reasonable to suggest that fTe2 in the F-JSZ environment was higher than in the MSZ environment, given the higher availability of Te in the F-JSZ sulphides (as discussed above).

![Figure 11. Chemical composition (atomic percent) of melt-related phases in the WGC plotted on a dual-ternary diagram (Au-Bi-S+Se-Te).](image-url)

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**Author:**

**Title:**

**Publication:**

**Volume:**

**Issue:**

**Pages:**

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**References:**

[5,18,33,73]
Based on the available data, the differences in composition between the F-JSZ and MSZ assemblages are best explained as a reflection of the composition of the pyrite and arsenopyrite most abundant in each spatial environment, with greater concentrations of Te and lower concentrations of Bi in the F-JSZ sulphides, which resulted in higher $f$Te$_2$ in the hydrothermal fluids associated with the melt event. It is possible that differences in $f$O$_2$-$a$H$_2$S between the footwall of the JSZ and the MSZ also impacted the composition of the LMCE phases, but gangue mineral assemblages in the two environments are similar and do not confirm deposit-scale variability in these parameters at the time of melt formation.

5.4. Melt Formation

The data, arguments, and conclusions presented thus far favour a model in which the F-JSZ and MSZ assemblages formed from polymetallic melts and that their constituent metals (Au, Bi, and Te) were scavenged from pre-existing pyrite and arsenopyrite in the WGC, such that the bulk compositions of the F-JSZ and MSZ assemblages were influenced by the trace-metals content of pre-existing pyrite and arsenopyrite in different parts of the WGC. One fundamental question that has yet to be addressed is why the polymetallic melts formed at all. To this end, it is important to consider the experimental work of Tooth [6], which highlighted the role of chemical reactions at mineral–fluid interfaces in mediating physicochemical conditions (e.g., $f$O$_2$, $a$H$_2$S) that affect melt stability. For example, these researchers determined that the oxidation of Fe$^{2+}$ in pyrrhotite to form Fe$^{3+}$ in magnetite was coupled with the reduction of Bi$^{3+}$ in aqueous Bi(OH)$_3$ in order to form molten Bi$^0$. Such processes have also been described in natural samples. Cockerton and Tomkins [25] suggested that the reduction of aqueous Bi$^{3+}$ to molten Bi$^0$ was coupled with the oxidation of aqueous Fe$^{2+}$ to Fe$^{3+}$ to form magnetite, andradite, and/or epidote during the precipitation of these phases at the Stormont skarn deposit in Tasmania. At the Welatam prospect in Myanmar, Wang et al. [74] linked Bi melt formation to various fluid–mineral redox reactions involving pyrrhotite, magnetite, and molybdenite, and noted the role of molybdenite in providing catalytic surfaces that attracted aqueous Bi$^{3+}$.

In the WGC, Au-Bi-Te minerals typically occur with siderite and, in some cases, Py$_4^-$ assemblages that are consistently proximal (within a few centimetres) to blebs of Py$_3^-$ and pyrrhotite in D$_3$ veins. The grain boundaries between siderite and Py$_3^-$ are irregular (Figure 4h–l) and are interpreted to represent the replacement of Py$_3^-$ by siderite. Based on the studies mentioned above and given the intimate association between Au-Bi-Te assemblages and siderite that replaced Py$_3^-$ in the WGC samples, an evaluation of the pyrite-siderite reaction is warranted to determine if this fluid–mineral reaction interface could have influenced the stability of the polymetallic melts.

5.4.1. Evolution of the System during the Replacement of Py$_3^-$ by Siderite

The architecture of the siderite + Py$_4^-$ coronae that formed at the expense of Py$_3^-$ is typified by the presence of Py$_4^-$ in the exterior part of the siderite rim and its absence in the interior part of the siderite rim, as displayed in Figure 4j. In assessing this reaction, the following assumptions are made: (1) the outer edge of the siderite + Py$_4^-$ coronae represents the original extent of Py$_3^-$ and pyrrhotite in D$_3$ veins. The grain boundaries between siderite and Py$_3^-$ are irregular (Figure 4h–l) and are interpreted to represent the replacement of Py$_3^-$ by siderite. Based on the studies mentioned above and given the intimate association between Au-Bi-Te assemblages and siderite that replaced Py$_3^-$ in the WGC samples, an evaluation of the pyrite-siderite reaction is warranted to determine if this fluid–mineral reaction interface could have influenced the stability of the polymetallic melts.
Figure 12. Cartoon illustrating the interpreted evolution of the pyrite–siderite replacement reaction with time. The blue arrows denote the direction of the progression of the hydrothermal fluid (starting from the outer rim of the Py3B bleb and moving inwards). The number of blue arrows corresponds to the relative amount of hydrothermal fluid in the system (and thus fluid flux, as discussed in the text). The sketch is based on the image presented in Figure 4j. See text for descriptions of each stage (a–d).

These stages can be further described in the context of chemical reactions that represent the replacement of Py3B by siderite. The following theoretical reaction is used to describe t1:

$$2\text{FeS}_2 (\text{Py3B}) + \text{HCO}_3^- + \text{H}^+ \rightarrow \text{FeS}_2 (\text{Py4}) + \text{FeCO}_3 + 2\text{HS}^- \quad (\text{R1})$$

The conversion of pyrite to siderite (transfer of Fe$^{2+}$ to siderite) and the release of S to solution as HS$^-$ requires the presence of some reduced S released from Py3B. Reaction (1) is not balanced with respect to the valences of the elements involved as the exact nature of the reducing agent is unknown. There are several candidates for reducing agents (e.g., CH$_4$, Fe$^{2+}$), but these were not incorporated given the absence of direct constraints on fluid chemistry. Note that HCO$_3^-$ and H$^+$ are aqueous species introduced to the system by the hydrothermal fluid derived from or having interacted with the lamprophyre dikes. During t1 (Figure 12b), fluid flux was relatively low and euhedral grains of Py4 crystallized with siderite, suggesting chemical equilibrium. Py3B, however, was not stable during this time, which may have related to differences in the trace-element compositions of Py3B and Py4 (see Figure 9, [35]), which is a factor known to affect the relative stabilities of minerals of the same species [75]. As fluid influx increased (t2; Figure 12c), the availability of HCO$_3^-$ increased, and neither type of pyrite was stable. Siderite therefore precipitated without Py4, as can be illustrated by the following theoretical reaction:

$$\text{FeS}_2 (\text{Py3B}) + \text{HCO}_3^- + \text{H}^+ \rightarrow \text{FeCO}_3 + 2\text{HS}^- \quad (\text{R2})$$

As with Reaction (1), and for the same reasons, Reaction (2) is not charge-balanced. An increase in fluid flux during t2 would also have decreased aH$_2$S, as aqueous HS$^-$ was transported out of the system. As fluid flux diminished, the availability of HCO$_3^-$ would have decreased and the reaction would have eventually ceased.
5.4.2. The Formation and Mediation of Melts at Py3B-Siderite Reaction Interfaces

During t1, pyrite was stable as Py4. F-JSZ assemblages coexist with Py4 and siderite (Figure 6d), and these minerals have Bi ≤ (Te + Se + S). In contrast, minerals of the MSZ assemblages, with Bi ≥ (Te + Se + S), should not stably coexist with pyrite [5], and indeed these minerals are not seen with Py4. It is likely, therefore, that the relatively Te-rich character of the fluids that migrated through the extensional vein network in the footwall of the JSZ (corresponding to higher $f_{Te2}$) stabilized melts with a bulk composition of Bi $\approx$ Te $>$ Au, which precipitated during t1. In contrast, the relatively Te-poor character of fluids that circulated in the studied samples of the MSZ (corresponding to lower $f_{Te2}$) prevented precipitation of polymetallic melts during t1. During t2, an increased fluid flux may have removed S from the system, consistent with neither Py3B nor Py4 being stable, which relates to the lack of Py4 in the interior part of the siderite domain. Under conditions of lower $aH_2S$, melts with a bulk composition of Bi $>$ Au $>$ Te would have been stabilized and able to form the MSZ assemblages. During t3, a decrease in fluid flux would have decreased the amount of S that was transported out of the system during Py3B dissolution. Although Py4 did not precipitate during t3, the occurrence of bismuthinite after bismuth in the MSZ (Figure 7e) and of S-rich tetradymite after tsumoite in the footwall of the JSZ (Figure 6e) point to higher $aH_2S$ in the system during t3 as opposed to t2. These stages are illustrated schematically in Figure 13.

<table>
<thead>
<tr>
<th>Stage</th>
<th>$t_0$</th>
<th>$t_1$</th>
<th>$t_2$</th>
<th>$t_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction</td>
<td>2FeS$_2$ (Py4) + HCO$_3^-$ + H$^+$ $\rightarrow$ FeS$_2$ (Py4) + FeCO$_3^- + 2H_2S^-$</td>
<td>FeS$_2$ (Py4B) + HCO$_3^-$ + H$^+$ $\rightarrow$ FeCO$_3^- + 2H_2S^-$</td>
<td>FeS$_2$ (Py4B) + HCO$_3^-$ + H$^+$ $\rightarrow$ FeCO$_3^- + 2H_2S^-$</td>
<td></td>
</tr>
<tr>
<td>Fluid flux</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>Moderate</td>
</tr>
<tr>
<td>$aH_2S$</td>
<td>High</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
</tbody>
</table>

![Figure 13. Cartoon illustrating a model of formation for Bi-Te-Au-bearing melts in F-JSZ and MSZ assemblages, as a function of the pyrite–siderite reaction interface, hydrothermal fluid flux, and differences in $f_{Te2}$. The blue arrows represent the magnitude of hydrothermal fluid input (fluid flux). The red blebs represent melt-related Au-Bi-Te phases in each group of assemblages, and the green blebs in the last image represent tetradymite for the F-JSZ assemblages and bismuthinite for the MSZ assemblages.](image-url)
An elusive piece of the puzzle is the direct effect, if any, of the Py$_{3B}$-siderite replacement reaction on the conversion of aqueous Bi$^{3+}$, the most likely oxidation state for aqueous Bi [76], to molten Bi$^0$. There is no direct evidence (i.e., mineral phases) of changes in the oxidation states of any of the other species in the system. It is quite possible that relatively reduced aqueous species participated in the reaction (i.e., were oxidized) without precipitating a phase that directly records their presence. An obvious contender is methane, which has been documented in several populations of fluid inclusions in the WGC [39] and contains reduced C that could have been oxidized to form siderite. A hypothetical reaction based on this is proposed below:

$$2\text{Bi(OH)}_3(aq) + \text{CH}_4(aq) + \text{FeS}_2 \text{ (Py}_{3B}) \rightarrow 2\text{Bi}(l) + 2\text{FeCO}_3 + 2\text{H}_2\text{S(aq)} + 3\text{H}_2\text{O} \quad (R3)$$

Note that the stability ranges of both CO$_2$ and CH$_4$ overlap with that of Bi$^0$ under $f\text{O}_2$-$a\text{H}_2\text{S}$ conditions typical of orogenic systems (Figure 14). It is also possible that some Fe$^{2+}$ or S$^{2-}$/$S^{0}$ from pyrite was oxidized to form Fe$^{3+}$ or S$^{6+}$, respectively, neither of which were incorporated into a solid phase. The D$_3$ veins also contain accessory to minor amounts of tourmaline and chlorite, both of which contain redox-sensitive elements (e.g., Fe) that could have acted as reducing agents for aqueous Bi$^{3+}$ (although no petrographic evidence for such reactions was observed in the studied samples). If the chemical reaction involving the reduction of aqueous Bi$^{3+}$ comprised exclusively aqueous species, it can be posited that the pyrite–siderite reaction front simply facilitated conditions favourable to the formation of melts, as described above. Once formed, the polymetallic melts, whether Bi ≈ Te > Au or Bi > Au >> Te in composition, would have effectively scavenged Au from the coexisting hydrothermal fluids and subsequently precipitated gold.

![Figure 14](image-url)  
**Figure 14.** Stabilities of various species in $f\text{O}_2$-$a\text{H}_2\text{S}$ space at conditions reasonable for orogenic deposits. The phase diagram is drawn after thermodynamic data presented and discussed in [6].

5.5. The Role of Bi-Rich Polymetallic Melts in the WGC and Other Orogenic Au Systems

When considering the impact of polymetallic melts on Au mineralization in the WGC, it is noted that they were not responsible for the introduction of Au to the deposit, nor for its deposit-scale redistribution (i.e., from the various sulphide minerals in the shear zones and host rocks to the D$_3$ veins). Although trails of globular Au-Bi blebs (cf. Figure 7d) and the emplacement of Bi phases along grain boundaries and fractures in D$_3$ vein quartz (cf. Figure 7f) suggest some amount of melt migration after formation, all the observed assemblages are within a few centimetres of sulphide blebs and no melt assemblages
have been so far conclusively documented outside of the D₃ veins (e.g., in the schists that constitute the various shear zones, or their less-deformed host rocks). It could be posited that the melts formed outside of the D₃ veins and that the pyrite–siderite reaction fronts in these veins triggered the crystallization of solid phases from the melts (rather than the formation of the melts themselves), but it seems unlikely that deposit-scale melt migration could have occurred without precipitating solid LMCE phases throughout the deposit. Given the consistent spatial relationship between the melt assemblages and the D₃ veins, the hypothesis that the melts formed in the veins themselves is preferred. Thus, Bi-rich polymetallic melts in the WGC played a role in concentrating gold in the D₃ veins (via partitioning from the coexisting hydrothermal fluids), resulting in high-grade (often 10 s of g/t) mineralized zones, but the deposit-scale mass transfer of Au, Bi, and Te from the sulphides disseminated in the Jubilee Stock and shear zones to the D₃ veins was the result of hydrothermal fluid–rock interactions.

An apparent consistency between the WGC model and those presented for other orogenic or shear zone-hosted lode Au deposits where gold has in part been attributed to crystallization from Bi-rich melts is the formation of these melt assemblages after the crystallization of Fe or Fe-As sulphides [7,17–21,77]. In some deposits, paragenetically earlier sulphides were postulated to be the source of Au for later Bi-rich melts [7,17,21], whereas in other settings no direct link is made between early sulphide mineralization and later precipitation of gold and LMCE minerals from a melt phase. The commonality of this paragenesis (i.e., the formation of polymetallic melts after primary Au + sulphide mineralization) is sensible considering that most orogenic hydrothermal fluids are pyrite-stable [78,79], which reflects $a\text{H}_2\text{S}/f\text{O}_2$ conditions incompatible with molten Bi [5,6] (Figure 13), and the potential of these sulphides in sourcing trace metals and providing micro-environments that promote melt formation [6,74]. Indeed, this study joins several others in refining the role of Bi-rich melting in natural orogenic Au systems as one of gold redistribution, rather than introduction [7,17,21]. In the current work, a more detailed understanding of how Au, Bi, and Te were redistributed, both in terms of process (hydrothermal vs. melt) and scale (deposit-scale vs. centimetre-scale) was possible through the trace-element analysis of sulphide minerals (e.g., pyrite and arsenopyrite) and subsequent mass–balance calculations. This approach (mass–balance calculations based on trace-element contents in sulphides, as analysed by LA-ICP-MS) is regularly used to help determine how Au moves in orogenic deposits during primary (i.e., introduction) and secondary (i.e., redistribution) mineralisation events in orogenic systems [7,35,80,81]. Extending the assessment to Bi and Te in deposits where LMCE melts have been identified will help to evaluate which sulphides (if any) could have sourced the metals that constitute the melts, and, in conjunction with textural and paragenetic constraints, allow for assessments of the scale and impact of mobilization to be made.

5.6. Using Element Associations to Identify Magmatic–Hydrothermal Contributions of Au

The two Au events that formed the WGC are distinguishable in terms of their geochemistry, mineralogy, and structural and paragenetic relationships. The first comprises disseminated gold and Au in solid solution in D₁ arsenopyrite and As-bearing pyrite in quartz + phyllosilicate + carbonate schists and veins, whereas the second comprises gold, Bi-Te-Au minerals, and chalcopyrite hosted in carbonate ± K-feldspar ± riebeckite ± chlorite veinlets that cut D₃ veins. The Au-Bi-Te(-Cu) association that defines the latter event is one that is often taken as evidence for a magmatic–hydrothermal source of Au-mineralizing fluids [18–23,34,74,77,82,83]. In the WGC, however, the hydrothermal fluids associated with the second Au event were probably related to the emplacement of Archean lamprophyric magmas that are unlikely to have added significant quantities of Au, Bi, and Te to the mineralized system. Instead, this magmatic–hydrothermal event was responsible for redistributing and upgrading pre-existing Au, Bi, and Te through a combination of hydrothermal transport and polymetallic melt formation. The association of these elements in the late assemblages of the WGC is not a product of hydrothermal
fluid source, but rather of their fractionation into LMCE melts. The WGC is therefore an example of how magmatic–hydrothermal fluids can overprint an orogenic deposit and form Au-Bi-Te mineral assemblages without contributing these elements, in particular Au, to the system. The distinction between mobilization of existing Au and introduction of new Au is paramount, particularly when considering the point that when Au-Bi-Te assemblages are observed in orogenic deposits, they typically post-date Au-As mineralisation [7,17–21,77]. An understanding of the timing of magmatic–hydrothermal fluid input with respect to existing Au mineralization, of the source of the magmatic–hydrothermal fluids and its potential to produce Au-enriched fluids, and of the nature and magnitude of existing Au mineralization is necessary to discriminate between these two scenarios (i.e., mobilization vs. introduction). Identification of a magmatic–hydrothermal contribution of Au based solely on an Au-Bi-Te(-Cu) association is cautioned, particularly in deposits where LMCE melts have been identified.

6. Conclusions
1. The formation of Bi-Te-Au melts in selected samples from the WGC was the product of deposit-scale mobilisation of these elements out of earlier sulphides, a process likely related to fluid circulation driven by the intrusion of Archean (2700–2670 Ma) lamprophyre dikes during the late stages of deformation. Melt composition was influenced by the geochemical environment in which the melts formed (i.e., proximity to abundant Te-rich sulphides in the JSZ footwall vs. the relatively Te-poor MSZ) and their precipitation and evolution was mediated by chemical reactions at fluid–pyrite–siderite reaction fronts.

2. The paragenetic relationship of the two Au mineralizing events in the WGC, these being an early Au-As event and a later Au-Bi-Te event, seems to be shared by many orogenic Au deposits in which polymetallic melt generation has been documented. The apparent consistency with which Bi-rich melts postdate primary Fe-sulphide + Au-As mineralisation probably relates to the relatively oxidized nature of the hydrothermal fluids that form these deposits (above the stability field of Bi\(^0\)) and the role of pre-existing sulphide mineralization in acting both as a potential source of Au and LMCEs and as favourable micro-environments for melt formation. The liquid-Bi collector model is evidently important in the upgrading of pre-existing Au mineralization but is probably not a feasible mechanism for the initial precipitation of gold in orogenic systems. Given the importance of sulphide minerals as repositories of Bi and Te in these systems, the use of trace-element analysis of such minerals in LMCE melt research may allow more complete understanding of such processes in natural systems.

3. Despite the importance of late magmatic-hydrothermal fluids in the formation of Au-Bi-Te assemblages in the WGC, it is unlikely that these fluids introduced significant amounts of new Au, Bi, and Te to the deposit. This work highlights the importance of discriminating between the mobilization of existing Au (and related elements) and the addition of new Au. This intricacy is fundamental to resolving the sources of Au-bearing fluids that form orogenic deposits.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/min13091119/s1: Table S1, comprising the SEM-EDS data discussed herein.

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Data Availability Statement: The complete LA-ICP-MS sulphide chemistry dataset discussed herein is associated with Wehrle et al. [35]. The SEM-EDS data discussed herein are available as Supplementary Material.

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