Comparison of decrepitation, microthermometric and compositional characteristics of fluid inclusions in barren and auriferous mesothermal quartz veins of the Cowra Creek Gold District, New South Wales, Australia

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Abstract

Fluid inclusions in quartz from barren and Au-sulfide-bearing veins from the Cowra Creek Gold District, New South Wales, Australia, have been characterized based on their decrepitation behavior and gas geochemistry. Inclusions in Au-sulfide veins, and some regional sulfide-bearing veins, show distinctly higher CO\(_2\)/CH\(_4\) ratios compared to barren quartz-only and quartz-sulfide veins from the deposit environment. Additionally, the occurrence of low-temperature peaks in acoustic decrepigrams from Au-sulfide veins that had previously been attributed to the presence of CO\(_2\)-bearing fluid inclusions has been confirmed using optical techniques. This characteristic peak is absent from quartz-sulfide and quartz-only veins. These results suggest that the gas content of fluid inclusions can distinguish Au-bearing from barren quartz veins, and that the acoustic decrepitation technique may provide a rapid and simple means of identifying different generations of quartz, and potentially productive veins in mesothermal environments.

1. Introduction

The development of successful exploration strategies to search for hydrothermal mineral deposits requires techniques which may be used to rapidly and inexpensively discriminate between barren and potentially productive systems. For many years, fluid inclusions have been used successfully to determine the type of hydrothermal system being investigated and where in the system, relative to ore, the sample is from. For example, the presence of fluid inclusions showing evidence of boiling in a quartz vein from a surface outcrop in an epithermal precious metal prospect indicates that the highest grade Au–Ag mineralization, if present, lies at some depth below the surface, justifying allocation of expenditures for a drill hole (Bodnar et al., 1985; Bodnar, 1988, 1992). Similarly, the presence of halite-bearing fluid inclusions in a sample from a porphyry copper prospect indicates that the sample is from the central portion of the hydrothermal system that hosts...
the ore shell (Bodnar, 1982). Further, the presence of chalcopyrite daughter minerals in these same or other inclusions in the sample indicates that the hydrothermal fluids were metalliferous and that economic mineralization is more likely than if the inclusions were metal-poor (Beane and Bodnar, 1995). Often, fluid inclusion characteristics can effectively identify the type of hydrothermal system or the ore environment being studied, even when alteration or other features are ambiguous or absent. Thus, Beane and Bodnar (1995) describe how fluid inclusion characteristics discriminate between quartz veins in propylitic alteration peripheral to a porphyry copper deposit and similar alteration associated with epithermal precious metal systems. These same authors describe the application of fluid inclusions in tropical, heavily weathered or vegetated areas where conventional alteration mapping is not possible.

In addition to the deposits mentioned above, mesothermal turbidite- and greenstone-hosted Au deposits are appropriate systems in which to use fluid inclusions as an exploration tool. As a result of numerous fluid inclusion and other geochemical studies over the past decade, the presence of CO2-rich fluids is unanimously accepted as characteristic of these types of gold deposits. The CO2-gold association ranges from the depositscale (Groves et al., 1989; Kishida and Kerrich, 1987; Wood et al., 1986) to the thin-section-scale (Boullier and Robert, 1992; Diamond, 1990; Robert and Brown, 1986; Robert and Kelly, 1987). Moreover, the close spatial relationship between mesothermal gold mineralization and CO2-rich inclusions suggests that the presence of these inclusions can be used as an exploration tool in the search for this important class of deposit. Thus, Diamond and Marshall (1990) demonstrated that simple crushing stage examinations to test for the presence of CO2-bearing fluid inclusions help identify potentially auriferous quartz veins. Similarly, Smith and Kesler (1985) used GC analyses of fluid inclusions to document a CO2 halo around the Hollinger–McIntyre gold mine in Timmins Ontario. It should be noted that different camps often display different fluid inclusion characteristics. For example, in their study of the quartz veins associated with the Sigma mine Val d’Or, Quebec, Sherlock et al. (1993) found that fluid inclusions from auriferous veins contained CH4, while barren veins did not. However, it is generally the case that high density CO2 fluid inclusions are associated with mesothermal Au-bearing quartz veins. Ho (1987) documented that all the Archean mesothermal gold deposits of Western Australia contain abundant CO2-rich fluid inclusions, frequently displaying two CO2 phases at room temperature.

Accepting the fact that CO2-rich fluid inclusions are characteristic of the mesothermal gold–quartz veins, the presence of such inclusions may be used as a favorable feature in the search for new occurrences. In areas of multi-stage quartz veining, it may also be possible to use relative CO2 content to distinguish different generations of veins, including the most favorable Au-mineralized vein sets. The presence of CO2-rich inclusions may be presumed or confirmed using a variety of techniques, including optical examination of fluid inclusions in thin or polished section, crushing studies on inclusions while they are observed under the microscope, microanalysis of inclusions using techniques such as gas chromatography, mass spectrometry, Raman spectroscopy, etc., and acoustic decrepitation. Any or all of these techniques are well-suited for the identification of CO2-rich fluid inclusions. Unfortunately, most of these techniques are unsuitable for use in mineral exploration, where throughput of a large number of samples rapidly and inexpensively, and by a relatively inexperienced operator, is necessary. For these reasons, the acoustic decrepitation technique may be the most desirable of the various techniques.

Various workers have proposed that acoustic decrepitation characteristics of fluid inclusions can successfully discriminate between barren quartz veins and those containing gold (e.g., Ho, 1987, Xie, 1989; Burlinson, 1991). Burlinson (1991) has documented the recognizable differences in the shapes of decrepigrams of barren versus mineralized mesothermal quartz veins and has attributed these differences to the presence of abundant, high density CO2-rich fluid inclusions in mineralized samples and their rarity in barren veins. This interpretation is reasonable, based on the ubiquitous presence of CO2 fluid inclusions in mesothermal gold deposits, but has not been tested by careful analysis of inclusions from the two different (mineralized vs. barren) vein types within a single district. The goal of this study was to test the hypothesis that the low-temperature peak in decrepigrams of Au-bearing quartz from mesothermal veins is related to the presence of CO2-rich fluid inclusions, and to compare inclusions
from quartz veins associated with gold mineralization with barren quartz veins in the same area.

The Cowarra gold deposit, located 200 km southwest of Sydney, Australia (Fig. 1), is the largest of a number of epigenetic lode gold systems which make up the Cowra Creek goldfield. The deposit is part of a north-south trending belt of mineralization, 1.5 km by 15 km long hosted by Ordovician slates and sandstones which have been metamorphosed to greenschist grade. Just east of the deposit (1.8 km) there is a narrow zone of higher grade metamorphic rocks including biotite-andalusite-bearing schists. The surrounding terrain is also intruded by Late Silurian to Early Devonian I-type granitoid plutons. The Cowarra deposit consists of a number of narrow anastomosing lodes composed of massive and irregular sulfide-quartz veins developed in dilational structures. These sulfide-rich veins contain mostly pyrite with minor pyrrhotite and arsenopyrite and trace amounts of chalcopyrite, galena, sphalerite, bismuth and Au. Au grades average 8–13 grams/ton. Total recorded production from the Cowarra deposit is 1063 kg of gold (Ho et al., 1995).

The Cowarra deposit was selected for this study because it contains a variety of quartz-bearing veins including: (1) Au-bearing, sulfide-quartz veins, (2) quartz veins with minor sulfides and little or no Au (<0.1 ppm) and (3) quartz veins with no sulfides or detectable gold. A detailed study of the structural controls and development of veins at the Cowarra deposit (Rickard et al., 1995) indicates that the quartz-rich veins can be grouped into seven distinct types or stages. These include early flat tension veins associated with folding (type I) and veins along cleavage (type II). These veins are not common in the immediate mine environment relative to later vein types. Type II veins occur as veinlets, lenses and thicker irregular veins in the shear zones, in some cases with minor sulfides. They are synchronous with, or slightly later than, the sulfide-rich veins that carry the gold mineralization. Later vein generations include: type IV which are large veins that cross-cut the mineralized shear zones and carry some remobilized sulfides; type V quartz rods developed at nodes to boudinaged greywacke beds or sulfide ore veins, also in some cases containing minor sulfides; type VI veins which form steep, E-W trending, cross-cutting veins commonly along the axial planes of late kinks; and type VII veins which generally form small, flat veins along moderately dipping late reverse faults. Most of the barren quartz-only and sulfide-quartz veins sampled in this study are later than the sulfide–gold mineralization (Table 1). The compositions of fluid inclusions within the vein types was characterized to define geochemical differences, if any, between mineralized and barren samples, and to identify why different vein types appear to produce distinctive acoustic decrepitation patterns. These results, in turn, may be used to develop more effective exploration strategies for mesothermal gold mineralization.

2. Procedures and results

A total of twelve samples collected from sulfide-quartz–Au, quartz–sulfide and quartz-only veins of the Cowarra gold mine were studied. Three replicates of each sample were made so that each split could be studied by a different technique. One split was analyzed using the acoustic decrepitation technique. Doubly polished thin sections were prepared from the second split for petrographic and microthermometric studies, and the third split was used for quadrupole mass spectroscopic analysis of the gases released from fluid inclusions. Combined, these techniques offer a unique view of mesothermal Au–quartz vein fluid geochemistry, as well as an opportunity to test each technique against the others.

2.1. Acoustically monitored decrepitation

One split of each sample was heated while audio output generated by inclusion decrepitation was mon-
Table 1
Cowarra sample analysis record

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Vein type</th>
<th>Vein stage</th>
<th>Acoustic decrepigram</th>
<th>Visual decrepigram</th>
<th>Mass spectrometric</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Qtz-only</td>
<td>VII</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Qtz-only</td>
<td>III</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Qtz-only</td>
<td>IV</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Qtz-only</td>
<td>VII</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Qtz-only</td>
<td>V</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Qtz-only</td>
<td>regional–early</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Qtz–sulfide</td>
<td>regional–late</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Qtz-only</td>
<td>regional</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Qtz–sulfide</td>
<td>IV</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Qtz–sulfide</td>
<td>IV</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Sulfide–qtz–Au</td>
<td>III (in lodes)</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Qtz–sulfide</td>
<td>III (in lodes)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>13</td>
<td>Sulfide–qtz–Au</td>
<td>III (in lodes)</td>
<td>X</td>
<td></td>
<td></td>
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<td>14</td>
<td>Sulfide–qtz–Au</td>
<td>III (in lodes)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>15</td>
<td>Sulfide–qtz–Au</td>
<td>III (in lodes)</td>
<td>X</td>
<td></td>
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</tr>
</tbody>
</table>

It is monitored, as described by Burlinson (1991). Twelve samples, including representatives of all three vein types (i.e., sulfide–quartz–Au, quartz–sulfide and quartz-only) were analyzed. Representative acoustic decrepigrams of Cowarra samples are presented in Fig. 2A, C and E. All samples show a large, distinct peak at the quartz α/β transition temperature (573°C). As is typical of mesothermal Au deposits, those samples containing sulfides and gold display a very large, broad, low temperature peak (Fig. 2A) centered at 340°C, and ranging from 180–500°C. The lower temperature peak at approximately 340°C has been attributed to the decrepitation of CO₂-ch fluid inclusions by Burlinson (1991). Note that the decrepigram (Fig. 2A) for quartz associated with gold mineralization is significantly different from those for quartz-rich veins containing no gold (Fig. 2C and E). Decrepigrams from quartz-only samples show a gently sloping background below the α/β transition (Fig. 2E). Quartz–sulfide samples show small indistinct peaks barely discernible above background (Fig. 2C).

2.2. Optically monitored decrepitation

Petrographic examination of the Cowarra quartz samples revealed multiple fluid inclusion generations of variable morphology and size. Although most of the samples were indistinguishable petrographically, the sulfide–quartz–Au samples contained more abundant large, regularly shaped fluid inclusions compared to quartz–sulfide or quartz-only samples. Since none of the inclusions showed the characteristic CO₂ “double-bubble” at room temperature, doubly polished sections were observed during cooling to −195°C and subsequent reheating to room temperature to test for the presence of CO₂ and other gases (Bodnar et al., 1985). Temperatures of various phase changes observed during heating were used to estimate the inclusion composition. On this basis, the following four types of fluid inclusions were identified in the Cowarra samples: (1) aqueous with no detectable gases; (2) aqueous–CO₂; (3) CO₂, and; (4) CO₂–CH₄. The presence or absence of CO₂ and/or CH₄ was confirmed by Raman analysis. Fluid inclusions in sulfide–quartz–Au veins are predominantly CO₂-bearing, while in the quartz–sulfide and quartz-only veins aqueous inclusions are the most abundant. Type 4 (CO₂–CH₄) inclusions were only observed in the quartz-only samples.

After compositions of individual inclusions were determined from microthermometric and/or Raman analysis, each inclusion was continuously observed during slow heating to the temperature of decrepitation (Td). In each small chip, several tens of inclusions were generally monitored during each heating run. Thus, paired composition–decrepitation data for each of approximately 1000 inclusions were obtained. Where possible, partial (CO₂ liquid and vapor) homogenization (Th,CO₂) and total homogenization (Th) were noted, but no relationship between Th and Td was found for the Cowarra samples. Because the
Fig. 2. Acoustic decrepigrams of sulfide-qtz-Au (A), quartz-sulfide (C) and quartz-only (E) samples, and histograms of decrepitation temperatures determined by visually monitoring individual inclusions from sulfide-qtz-Au (B), quartz-sulfide (D) and quartz-only (F) samples.
The decrepitation behavior of inclusions is strongly size dependent (Bodnar et al., 1989) decrepitation temperatures were obtained from a wide range of fluid inclusion sizes. However, fluid inclusions below approximately 4 μm were too small for reliable thermometric analysis. Therefore, our optical determination of the decrepitation temperature range of Cowarra fluid inclusions impart a size bias that is not applicable to the other techniques utilized in this study. That is, both the acoustic decrepitation and quadrupole mass spectrometric analyses record information from inclusions which were too small to be monitored optically. Because small inclusions decrepitate at a higher internal pressure (higher temperature) than larger inclusions of the same composition, our optically-determined decrepitation histograms should show maxima at a somewhat lower temperature than peaks on acoustically-determined decrepigrams which presumably include the more abundant smaller inclusions (Roedder, 1984).

The pure CO₂ (type 3) and the aqueous–CO₂ (type 2) inclusions show similar decrepitation behavior, and are grouped together and labelled CO₂–aqueous in Fig. 2B, D, and F. As with the acoustic decrepitation measurements, the quartz-only and quartz–sulfide samples show a major peak at the quartz α/β transition (573°C) (Fig. 2D and F). Surprisingly, there is no peak at the α/β transition for the sulfide–quartz–Au samples (Fig. 2B), possibly because this peak is due to inclusions too small for visual monitoring.

Sulfide–quartz–Au samples show a large characteristic peak centered at 240°C, ranging from 150 to 350°C (Fig. 2B). This distinct, low temperature peak is due to the decrepitation of CO₂-rich (type 2 & 3) fluid inclusions. Aqueous fluid inclusion decrepitation temperatures group around 350°C, thereby skewing the overall decrepigram to higher temperatures, and broadening the “low temperature” peak.

Aqueous (type 1) inclusions in the barren veins decrepitate over a range of temperatures (centered around 350°C) similar to aqueous inclusions in the sulfide–Au samples (Fig. 2E). However, CO₂-rich (type 2 & 3) fluid inclusions in barren veins do not show a distinct decrepitation peak. The CO₂–CH₄ (type 4) inclusions decrepitate between 200 and 400°C with no characteristic peak, effectively smoothing out the lower temperature region of the decrepigram (Fig. 2F) producing a wide, broad low temperature peak that is distinct from that of the Au-bearing samples.

2.3. Quadrupole mass spectrometer analyses

A VG Quadrupole SX600 mass spectrometer (QMS) with closed electron source operated at 50 volts, and a secondary electron multiplier detector at 2000 volts, was used to analyze gases extracted from the Cowarra samples. Inclusion fluids were released for analysis by crushing or thermal decrepitation.

Crushing release was used to analyze four representative Cowarra samples, and a quartz–sulfide vein from 1.5 km east of the mine area. It is not known whether or not the latter is associated with gold mineralization. Quadrupole mass spectrometric analyses confirm the results of the visual decrepitation study. Table 2 shows the results of those analyses, and the four types of veins are readily distinguished by the CO₂/CH₄ ratio, where the quartz-only veins have a low ratio (<0.1), the sulfide–quartz–Au and quartz–sulfide veins show

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vein stage</th>
<th>H₂O</th>
<th>CO₂</th>
<th>CH₄</th>
<th>N₂</th>
<th>Ar</th>
<th>H₂S</th>
<th>HCl</th>
<th>H₂</th>
<th>CO₂/CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfide–quartz–Au</td>
<td>III (in lodes)</td>
<td>84.3</td>
<td>10.2</td>
<td>4.7</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Qtz–sulfide</td>
<td>regional-scale</td>
<td>95.3</td>
<td>3.0</td>
<td>0.2</td>
<td>1.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>16.8</td>
</tr>
<tr>
<td>Qtz-only</td>
<td>IV</td>
<td>86.5</td>
<td>5.8</td>
<td>4.1</td>
<td>3.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.4</td>
</tr>
<tr>
<td>Qtz-only</td>
<td>V</td>
<td>59.1</td>
<td>8.5</td>
<td>25.6</td>
<td>6.3</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>
higher ratios (2.18 and 1.41 respectively) and the regional quartz-sulfide vein has the highest ratio (10.83). In the latter case the high CO₂/CH₄ ratio is due to the very low CH₄ content of these samples. A ternary plot of CO₂–CH₄–N₂ clearly distinguishes the four vein types (Fig. 3).

One sulfide-quartz-Au sample (#15) that contained sufficient numbers of large fluid inclusions to produce adequate amounts of gas was sequentially heated in order to facilitate QMS analyses of individual fluid inclusion bursts as temperature was increased. The results of this sequential heating run (Fig. 4) show that CO₂ release decreases as temperature increases. This presumably reflects the opening of the larger inclusions at lower temperature and smaller inclusions at higher temperature, with concomitantly less total gas being released with decreasing inclusion size.

3. Summary of results

Acoustic and visual decrepitation measurements both yield decrepigrams of similar overall form. In gold-bearing veins, both methods show significant peaks at low temperature (200–400°C), although the peak in the visually-determined decrepigrams occurs at somewhat lower temperatures than that for acoustically-determined decrepitation. This difference reflects the different ranges of inclusion sizes being monitored by the two techniques, with the average size from optical determinations being somewhat larger than that being measured acoustically.

Our results confirm the earlier conclusion of Burlinson (1991) that the intense peak in the low temperature region of the decrepigrams from Au-bearing quartz veins is due to the presence of abundant CO₂-rich inclusions. These inclusions are much less common in the quartz–sulfide and quartz-only veins. Comparison of the acoustic and optical decrepitation results confirms that the low temperature peak in both decrepigrams represents CO₂-rich inclusions. Furthermore, we have identified CO₂–CH₄ inclusions which are restricted to the quartz-only veins and which decrepitate over a wide range at temperatures ≤ 400°C. Acoustic decrepitation analysis thus provides a simple, rapid and inexpensive means of distinguishing different generations of quartz veins and identifying CO₂ rich, potentially mineralized veins in the Cowarra system. The technique thus represents a promising exploration tool that can be applied in mesothermal environments worldwide.

4. Conclusions

Our results support conclusions of previous studies concerning the close association of high-density, gas-bearing (in this case CO₂) fluid inclusions with Au-bearing quartz veins. Moreover, acoustic decrepitometry has been shown to be an effective, rapid and inexpensive technique for detecting these inclusions. We have shown that fluid inclusion chemistry and decrepitation behavior can be used to distinguish Au bearing from barren quartz veins in an area containing numerous generations of quartz veins. But, why should an exploration geologist analyze fluid inclusions when simple assays will tell her unequivocally which veins carry gold? The answer lies in the fact that assay
results can be misleading because of the nugget effect; Au grades may be spotty within one vein, with high grades in one portion and barren quartz a few meters away. Conversely, fluid inclusion assemblages are usually consistent over 10s to 1000s of meters, both vertically and horizontally, in a single vein. Thus, Au grades at one sample locality along a vein may not be promising, but the fluid inclusion characteristics at that same location would tell the explorationist that the vein has potential and that Au is likely to be present at other locations along the vein.

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References


Smith, T.J. and Kesler, S.E., 1985. Relation of fluid inclusion geochemistry to wallrock alteration and lithogeochemical zonation