40Ar/39Ar dating of mica-bearing pyrite from thermally overprinted Archean gold deposits

David Phillips
John M. Miller
School of Earth Sciences, Predictive Mineral Discovery Cooperative Research Centre (pmd*CRC),
University of Melbourne, Parkville, 3010 VIC, Australia

ABSTRACT
Previous studies have suggested that pyrite may armor potassium-bearing mineral inclusions from alteration-induced argon loss, thus providing improved 40Ar/39Ar age results. To test this hypothesis, matrix muscovite and pyrite crystals hosting muscovite inclusions were selected from two variably overprinted Yilgarn gold deposits (Western Australia) and analyzed by combined single crystal 40Ar/39Ar laser probe and “in vacuo” crushing methods. Pyrite grains from the ca. 2.60 Ga Mount Charlotte gold deposit exhibit evidence of minor argon loss, but give concordant high-temperature ages averaging 2594 ± 8 Ma (2σ), indistinguishable from previous age estimates. Matrix mica from the ca. 2.63 Ga Kanowna Belle gold deposit yielded a discordant age spectrum with all ages younger than 2.5 Ga, indicating substantial 40Ar* loss related to Middle Proterozoic thermal overprinting. Crushing and low-temperature heating experiments on pyrite crystals from Kanowna Belle produced anomalously old apparent ages (up to 7.0 Ga); however, in contrast to the matrix mica, total-gas pyrite ages generally approach or overlap the inferred time of gold mineralization. This behavior is attributed to diffusion of 40Ar* to internal muscovite-pyrite grain boundaries in response to the Middle Proterozoic thermal event, with limited external loss of argon. It is concluded that pyrite acts as a partially closed system for argon, but that the 40Ar/39Ar pyrite dating method has the potential to see through later thermal and/or alteration events and resolve controversial aspects of ore deposit geochronology.

Keywords: Archean, pyrite, gold, Yilgarn, Ar dating, Australia.

INTRODUCTION
Pyrite contains negligible structural potassium and would normally be a poor candidate for 40Ar/39Ar geochronology—unless it contains potassium-bearing mineral inclusions. The 40Ar/39Ar dating of pyrite was first attempted by York et al. (1982), who obtained an imprecise isochron age of 2500 ± 240 Ma (2σ) for analyses of bulk pyrite samples from the Archean Geoc sulfide deposit in Ontario, Canada. York et al. attributed the potassium and argon in pyrite to encapsulated silicate or fluid inclusions. Smith et al. (2001) used the 40Ar/39Ar laser probe method to analyze single pyrite grains from igneous intrusions in Brazil. These grains yielded ages similar to those of coexisting amphibole, suggesting that at least some pyrite samples can provide precise and reliable age information. The potassium content of the pyrite grains was attributed to the presence of microscopic inclusions of feldspar, amphibole, and phlogopite.

Although the results reported by Smith et al. (2001) are tantalizing, there has been no further application of the pyrite dating method. Possible reasons include the higher radioactivity of pyrite following neutron irradiation, compared to minerals typically used for 40Ar/39Ar dating; contamination of analytical lines by sulfur (e.g., poisoning of getters used for gas purification), leading to elevated system blanks; and the fact that there may be no incentive to date pyrite when coexisting potassium-rich minerals are present. Nonetheless, there are circumstances in which the dating of pyrite hosting potassium-bearing inclusions may be particularly useful. Smith et al. (2001) noted that phlogopite from one igneous intrusion yielded a younger age than either coexisting pyrite or amphibole, which they attributed to postcrystallization alteration, and concluded that pyrite protects potassium-bearing inclusions from alteration and may act as a time capsule, inhibiting both diffusive loss of 40Ar and recoil loss of 39Ar.

In this study we test the hypothesis that pyrite is capable ofarming potassium-bearing inclusions, and investigate whether the 40Ar/39Ar pyrite dating method can “see through” younger alteration and/or thermal events. We selected pyrite samples containing muscovite inclusions from two well-defined Archean gold deposits in Western Australia that have undergone variable degrees of hydrothermal and/or thermal overprinting.

GEOLOGY AND SAMPLE SELECTION
Gold-bearing pyrite samples were selected from the Mount Charlotte and Kanowna Belle deposits, both located in the Eastern Goldfields Province of the Yilgarn craton, Western Australia. The Eastern Goldfields Province is a Late Archean granite-greenstone terrane comprising deformed and metamorphosed volcanics and sediments intruded by granites and felsic volcanics (e.g., Witt, 1993; Groves et al., 1995). Gold mineralization is hosted by a variety of greenstones and generally postdates peak metamorphism (e.g., Yeats et al., 1999). Previous geochronological work on hydrothermal muscovite related to gold stockwork systems at Mount Charlotte yielded reproducible 40Ar/39Ar ages averaging 2602 ± 8 Ma (2σ), which were interpreted to represent the time of gold deposition (Kent and McDougall, 1995). The Kanowna Belle lode-gold deposit is dated by crosscutting felsic porphyry dikes to be younger than ca. 2655 Ma, with mineralization considered to have occurred ca. 2630 Ma, based on reset U-Pb zircon ages, Pb-Pb ages of ore-related galena, and an affinity with similar gold deposits in the region (Ross et al., 2004).

Sample MC1 was taken from a quartz stockwork vein at Mount Charlotte (drill hole MC263; 92 m) and comprises mainly quartz, muscovite (<0.15 mm), and pyrite (0.15–0.50 mm). This sample was selected to test the efficacy of the pyrite dating method on samples that exhibit only minor argon loss, as evidenced from analyses of MC1 matrix mica. Two samples, GD1 (drill hole GDD438; 351 m) and K1 (drill hole KDU1640; 200 m), were collected from the Kanowna Belle mine and also contain abundant muscovite (<0.15 mm) and pyrite (0.20–0.50 mm). The latter two samples were selected to determine the effects of Middle Proterozoic thermal events that have overprinted GD1 matrix muscovite. Pyrite grains from all three samples contain relatively coarse (to 0.15 mm) muscovite inclusions (Fig. 1), enabling direct comparisons with matrix muscovite from the same samples and also minimizing 39ArK recoil loss and/or redistribution problems.

ANALYTICAL METHODS AND RESULTS
Muscovite and pyrite separates from samples MC1, GD1, and K1, together with the flux monitors GA1550 (98.8 ± 0.5 Ma; Renne et al., 1998) and Hb3 (1072 Ma; Turner et al., 1971), were irradiated in position 5c of the McMaster Nuclear Reactor, Hamilton, Ontario. Muscovite step-heating analyses were conducted in a tantalum resistance furnace linked to a VG 3600 mass spectrometer equipped with a Daly detector. Laser step-heating and crushing analyses of pyrite crystals were achieved using a Spectron Nd-YAG laser and modified Nupro valve respectively, connected

© 2006 Geological Society of America. For permission to copy, contact Copyright Permissions, GSA, or editing@geosociety.org.
Fusion ages (Ma) and plateau ages for two samples from the Indian Ocean ridge:

Table 1. Summary of 40Ar/39Ar step-heating analytical results.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Mineral</th>
<th>Sample wt (mg)</th>
<th>No. grains</th>
<th>Low temp ages (Ma)</th>
<th>Fusion ages (Ma)</th>
<th>Total-gas age (Ma)</th>
<th>Plateau age (Ma)</th>
<th>Isochron age (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
<td>Minimum</td>
<td>Maximum</td>
<td>Minimum</td>
</tr>
<tr>
<td>Mount Charlotte</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC1</td>
<td>muscovite*</td>
<td>0.58</td>
<td>N.A.*</td>
<td>2033 ± 18</td>
<td>N.A.</td>
<td>2563 ± 14</td>
<td>N.A.</td>
<td>2654 ± 12</td>
</tr>
<tr>
<td>MC1</td>
<td>pyrite**</td>
<td>N.A.*</td>
<td>12</td>
<td>2052 ± 24</td>
<td>2604 ± 23</td>
<td>2578 ± 14</td>
<td>2626 ± 24</td>
<td>2550 ± 16</td>
</tr>
<tr>
<td>Kanowna Belle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GD1</td>
<td>muscovite*</td>
<td>0.97</td>
<td>N.A.</td>
<td>1605 ± 15</td>
<td>N.A.</td>
<td>2495 ± 11</td>
<td>N.A.</td>
<td>2594 ± 8</td>
</tr>
<tr>
<td>GD1</td>
<td>pyrite**</td>
<td>N.A.</td>
<td>15</td>
<td>2466 ± 14</td>
<td>4014 ± 18</td>
<td>1945 ± 52</td>
<td>2565 ± 14</td>
<td>2252 ± 20</td>
</tr>
<tr>
<td>K1</td>
<td>pyrite**</td>
<td>N.A.</td>
<td>14</td>
<td>2495 ± 44</td>
<td>4050 ± 39</td>
<td>2131 ± 12</td>
<td>2604 ± 16</td>
<td>2341 ± 24</td>
</tr>
</tbody>
</table>

Note: uncertainties in reported ages are at the two sigma level.

*Muscovite separates were heated incrementally from 500°C to 1450°C (15 and 24 steps, respectively).
*N.A. = not applicable.
**Single pyrite crystals (12–15 per sample) containing muscovite inclusions were laser step-heated in two to five increments.
to the surroundings through fractures, subsystem, in which some inclusions are exposed. It is well known that sulfide minerals such as pyrite retain noble gases, including helium (e.g., Turner and Stuart, 1992), which suggests that argon loss by volume diffusion through pyrite may not be the controlling mechanism for argon loss. Rather, it is suggested that pyrite behaves as a partially closed system, in which some inclusions are exposed to the surroundings through fractures, sub-grain boundaries, and/or by virtue of their location at pyrite grain boundaries (Fig. 4). Exposed inclusions, which are more susceptible to argon loss, are then preferentially out-gassed during initial heating of the pyrite, with argon from armored inclusions being released at higher temperatures. This explanation can account for both argon loss from pyrite and the discrepancy between the MC1 pyrite and muscovite apparent ages (younger than 2500 Ma) and time of gold mineralization (ca. 2630 Ma; Ross et al., 2004).

The discordant 40Ar* age spectrum for two single pyrite grains from samples GD1 and K1 (error boxes are 2σ), illustrating that most ages are intermediate between maximum matrix muscovite apparent ages (younger than 2500 Ma) and time of gold mineralization (ca. 2630 Ma; Ross et al., 2004).

Similar out-gassing behavior has been observed in 40Ar/39Ar studies of biotite inclusions in thermally overprinted garnet (Kelley et al., 1997) and for clinopyroxene inclusions in diamonds entrained in kimberlite magmas (Burgess et al., 1992). In both cases, 41Ar* was shown to accumulate along inclusion-host grain boundaries in response to postencapsulation heating, with gas loss only occurring on brittle failure of the host mineral and exposure of internal inclusion-host grain boundaries to the surroundings.

If the 40Ar* grain boundary component is retained quantitatively by the Kanowna Belle pyrite grains, then the total-gas ages should provide an estimate of the time of muscovite crystallization. However, as pyrite appears to be a variably closed system (Fig. 4), argon loss from exposed inclusions would be expected to yield younger ages ranging up to the time of mineralization. For samples GD1 and K1, all but two total-gas ages are similar to, or younger than, the inferred time of gold mineralization (ca. 2630 Ma). Of this group, the oldest five samples have a mean age of 2625 ± 9 Ma, within error of the preferred time of gold deposition (ca. 2630 Ma; Ross et al., 2004).

An alternative explanation for the anomalously old ages, obtained from crushing and low-temperature experiments on the Kanowna Belle pyrite samples, is release of excess 40Ar from fluid inclusions. Although we cannot totally discount contributions from fluid inclusions, the presence of excess argon is not supported because: (1) the majority of total-gas ages obtained from Kanowna Belle pyrite grains are similar or younger than the inferred time of gold mineralization; (2) pyrite from two widely separated samples from different structural zones in the Kanowna Belle deposit produced almost identical total-gas results; (3) K/Cl ratios for GD1 pyrite grains (~10–120) are poorly correlated with apparent age; and (4) Mount Charlotte pyrite grains contain negligible excess argon.

Excess argon contamination could, however, account for the two anomalously old Kanowna Belle pyrite grains (Fig. 3C), although...
incorporation of older detrital and/or xenocrystic inclusions in pyrite is also a possible explanation. In this regard, Dunlap (1997) demonstrated that detrital muscovite grains are able to survive greenschist facies metamorphism.

Many ore deposits, including orogenic gold systems, have proven extremely difficult to date in the past, due to multiple episodes of gold mineralization, postdepositional hydrothermal alteration events, and/or the presence of fine-grained white micas that are susceptible to recoil loss and/or redistribution of $^{39}\text{Ar}$ (e.g., Kerrich, 1994; Hanes et al., 1994; Witt et al., 1996; Kent and McDougall, 1996; Ferguson and Phillips, 2001). Building on the results of Smith et al. (2001), this study further highlights the potential of the pyrite dating method to ‘see through’ younger thermal events. Therefore, combined analyses of matrix mica and multiple mica-bearing pyrite grains could provide improved age constraints for many hydrothermally overprinted gold systems, and give new insights into controversies surrounding the age of deposits such as Val D’Or in Canada (e.g., Kerrich, 1994; Hanes et al., 1994).

REFERENCES CITED


Printed in USA

GEOLGY, May 2006