Development of Framboidal Pyrite During Diagenesis, Low-Grade Regional Metamorphism, and Hydrothermal Alteration*

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Abstract

Distribution patterns, microstructural relationships, and compositional variations for framboidal pyrite in the Paleozoic sedimentary host rocks to gold deposits on the northern Carlin trend, Nevada, and at Fosterville in central Victoria, collectively demonstrate that it is not all of synsedimentary-early diagenetic origin. Framboidal pyrite also nucleated in hydrothermal veins formed at several kilometers depth and along dissolution surfaces (stylolites and crenulation cleavages) formed during metamorphism at up to anchizonal grade (i.e., prehnite-pumpellyite facies). There are no obvious differences in either the size range or internal morphology of framboids formed in these various settings, suggesting that a single, relatively simple crystallization path may operate over a wide depth range in the upper crust. At Fosterville, anomalously metal-rich (including Au) framboidal pyrite is most abundant adjacent to laminated shear veins that developed by slip along bedding surfaces during folding of the sedimentary host rocks. Microstructural relationships and Pb isotope compositions for the framboidal pyrite, and other similarly distributed, early-formed sulfides, support development in response to the localized, episodic influx of metal-enriched H2S-bearing hydrothermal fluids during regional deformation between 440 and 400 Ma. These findings may have implications for other similarly deformed metasedimentary successions, where the discovery of Au-bearing framboidal pyrite has recently been cited as evidence for significant Au enrichment during sedimentation.

Introduction

Few mineral textures have been the subject of such prolonged and detailed study as framboidal pyrite (e.g., Schniederhöhn, 1923; Rust, 1935; Schouten, 1946; Love and Amstutz, 1966; Berner, 1970; Rickard, 1970, 1975; Sweeney and Kaplan, 1973; Raiswell, 1982; Morse and Cornwell, 1987; Wilkin et al., 1996, 1997; Wilkin and Barnes, 1997; Sawlowicz, 2000; Butler and Rickard, 2000; Ohfuji and Rickard, 2005; Ohfuji et al., 2005, 2006; Raiswell et al., 2008). Ohfuji and Rickard (2005) defined framboids as microscopic, spherical to subspherical clusters of equidimensional and equiatomic microcrystals. Individual pyrite framboids are generally 5 to 20 µm in diameter. They typically contain 103 to 106 microcrystals, which are 0.1 to 20 µm in size but usually <2 µm in diameter (Love and Amstutz, 1966; Rickard, 1970; Wilkin et al., 1996; Sawlowicz, 2000; Ohfuji and Rickard, 2005). Microcrystals may be loosely packed and randomly oriented or densely packed and highly ordered, and pyrite can form anywhere between approximately 10 and 75 percent of the framboid volume (Rickard, 1970; Wilkin et al., 1996). X-ray and electron backscatter diffraction studies by Ohfuji et al. (2005, 2006) demonstrate that greater morphological ordering is reflected in greater uniformity in crystallographic orientation of the microcrystals.

Numerous studies of modern marine and nonmarine sediments demonstrate that framboidal pyrite forms readily, with production rates commonly at a maximum, within centimeters of the sediment-water interface, due to interaction between bacterially produced H2S and detrital Fe minerals in the sediment (e.g., Love, 1967; Berner, 1970, 1984; Canfield et al., 1992; Wilkin et al., 1996; Raiswell and Canfield, 1998). In euxinic basins, where H2S is present in the water column, framboidal pyrite may also form above the sediment-water interface (Raiswell and Berner, 1985; Skei, 1988; Wilkin et al., 1996, 1997). Framboidal pyrite is also associated with certain hydrothermal ore deposits, although many of these are known or interpreted to have formed at, or near, the sea floor (e.g., Rickard and Zweifel, 1975; Honnorez et al., 1976; Chen, 1978; England and Ostwald, 1993; Hallbach et al., 1993; Pichler et al., 1999). Thus, while it is recognized that the formation of framboidal pyrite is not restricted to sedimentary environments, it is generally interpreted to be indicative of very shallow and relatively low temperature settings (e.g., <200°C, Rickard, 1970; Wilkin and Barnes, 1997).

To date, only a few studies provide examples of framboidal pyrite likely to have formed at significantly greater depth. Reedman et al. (1985) interpreted framboidal pyrite in quartz-pyrite-base metal veins from the Ordovician Snowdon Volcanic Group, North Wales to have formed at around 2-km depth. Framboidal pyrite in bitumen veins hosted by fractured lower Cretaceous rhyolite and andesite at the El Soldado Manto-type deposit in Chile is also interpreted to have formed at 2- to 3-km depth (Wilson and Zentilli, 1999; Wilson et al., 2003). Framboidal pyrite developed in, or spatially related to, hydrothermal veins has also been reported from Cambro-Ordovician shale at the Acton Vale quarry, Quebec (Sassano and Schrjiver, 1989), Upper Ordovician black shale at Dolancooth Gold Mine, Wales (Amnels and Roberts, 1989), as well as in some Cornish tin deposits (Schouten, 1946).

Where framboidal pyrite is preferentially (or exclusively) developed in veins (e.g., Reedman et al., 1985; Sassano and...
Solutions for paragenetically and microstructurally constrained pyrite and galena from Fosterville were determined by ICP-MS, using both the Agilent quadrupole ICP-MS at the University of Tasmania and the Nu Plasma multicollector ICP-MS (MC-ICPMS) at the University of Melbourne. Initial analyses were performed using the quadrupole instrument connected to a 213-nm solid-state laser, following procedures described by Meffre et al. (2008). Where possible, results were checked using the higher precision MC-ICPMS instrument following methods described in Woodhead et al. (2009).

To compensate for the lower analytical precision of the quadrupole ICP-MS, weighted averages for multiple analyses (typically 12) of texturally or microstructurally similar pyrite were determined using Ludwig’s (2003) Isoplot software. Poor results were obtained for two samples in which aggregates of framboidal pyrite were partly filled in and/or replaced by galena. Poor data quality was due to large fluctuations in Pb count rates, which could not be maintained in the optimum range for the quadrupole instrument (i.e., 40,000–5,000,000 cps for 208Pb, e.g., Meffre et al., 2008). The high Pb content of these samples precluded laser ablation analysis using the MC-ICPMS. However, galena from one of the samples (sample RHD019_161.56 m) was dissolved in a drop of concentrated HCl, after first cleaning the sample surface with double-distilled water. The acid was extracted by pipette and rinsed out with double-distilled water. The residue left after evaporation of the liquid was dissolved in 2 percent HNO3 for analysis by solution ICPMS using the quadrupole instrument. The Pb isotope composition determined for the galena is the average of ten repeat analyses of the sample solution. Data were corrected for mass bias against a primary standard and galena from Que River, western Tasmania, analyzed by the same procedure, provided a secondary standard.

Framboidal Pyrite from the Northern Carlin Trend, Nevada

Framboidal pyrite is widely preserved in the Devonian sedimentary rocks that are the main hosts to gold deposits on the northern Carlin trend. Samples described here come from the upper Popovich and overlying Rodeo Creek Formations. Both units were deposited in outer carbonate shelf to basinal settings and consist of variably carbonaceous and pyritic, dolomitic, to locally siliceous siltstone and shale, with lesser interbedded calcarenite and liothlastic to bioclastic debris flows (Armstrong et al., 1998; Furley, 2001; Scott et al., in prep.). During Early Mississippian emplacement of the now overlying Roberts Mountains allochthon, these strata passed through the oil generation window, and numerous hydrocarbon-filled veinlets (now pyritobunten or graphite) formed in and adjacent to originally organic-rich rocks (Kuehn and Rose, 1992; Emsbo and Koenig, 2007). These veinlets are particularly useful to pyrite paragenetic studies, as crosscutting relationships provide a basis for discriminating early diagenetic pyrite (i.e., prehydrocarbon generation) and later diagenetic and/or hydrothermal pyrite (Scott et al., in prep.).

Framboidal pyrite of interpreted early diagenetic origin

Framboidal pyrite of interpreted synsedimentary to early diagenetic origin occurs throughout the Popovich and Rodeo Creek Formations, however, it is best developed in the Soft-Sediment Deformation unit and basal part of the overlying
Table 1. Selected LA-ICPMS Trace Element Data (ppm)

<table>
<thead>
<tr>
<th>Analysis Type</th>
<th>Al</th>
<th>V</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>As</th>
<th>Se</th>
<th>Mo</th>
<th>Ag</th>
<th>Sb</th>
<th>Au</th>
<th>Th</th>
<th>U</th>
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<tr>
<td>CD12c (852.6 ft), Goldstrike, northern Carlin trend</td>
<td>3357</td>
<td>49</td>
<td>2</td>
<td>492</td>
<td>147</td>
<td>307</td>
<td>180</td>
<td>271</td>
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<td>74</td>
<td>&lt;0.92</td>
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<td>68</td>
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<td>&lt;43</td>
<td>40</td>
<td>&lt;2</td>
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<td>10</td>
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<td>88970</td>
<td>&lt;43</td>
<td>42</td>
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<td>29541</td>
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<td>89</td>
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<tr>
<td>OC09A09a Outer colloform mc/py</td>
<td>1753</td>
<td>3</td>
<td>2</td>
<td>54</td>
<td>42</td>
<td>301</td>
<td>5</td>
<td>61</td>
<td>0.7</td>
<td>40</td>
<td>0.03</td>
<td>3.1</td>
<td>95</td>
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<tr>
<td>OC09A09c Framboid dominant</td>
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<td>54</td>
<td>183</td>
<td>182</td>
<td>171</td>
<td>&lt;17</td>
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<td>1666</td>
<td>553</td>
<td>1174</td>
<td>3107</td>
<td>26</td>
<td>112</td>
<td>20.4</td>
<td>592</td>
<td>1.72</td>
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<td>6069</td>
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<tr>
<td>JN28A92 Pre-S2 fram aggregate</td>
<td>10989</td>
<td>10</td>
<td>1666</td>
<td>553</td>
<td>1174</td>
<td>3107</td>
<td>26</td>
<td>112</td>
<td>20.4</td>
<td>592</td>
<td>1.72</td>
<td>0.7</td>
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<td>49883</td>
<td>196</td>
<td>1012</td>
<td>1017</td>
<td>629</td>
<td>1051</td>
<td>&lt;24</td>
<td>&lt;12</td>
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<td>444</td>
<td>&lt;0.65</td>
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<td>375</td>
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<tr>
<td>JN28A107 Pre-S2 fram</td>
<td>77</td>
<td>&lt;1</td>
<td>1490</td>
<td>395</td>
<td>401</td>
<td>1146</td>
<td>&lt;68</td>
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<tr>
<td>JN28A115 Pre-S2 f.g. py</td>
<td>154</td>
<td>&lt;1</td>
<td>903</td>
<td>458</td>
<td>1025</td>
<td>1700</td>
<td>26</td>
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<td>211</td>
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<td>DALD017 (66.25 m), Daly’s Hill area, Fosterville</td>
<td>524</td>
<td>1</td>
<td>38</td>
<td>556</td>
<td>138</td>
<td>1191</td>
<td>16</td>
<td>110</td>
<td>5.0</td>
<td>223</td>
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<td>216</td>
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<tr>
<td>NO08A04 Pre-S2 cluster f.g. py</td>
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<td>1</td>
<td>1</td>
<td>62</td>
<td>31</td>
<td>4069</td>
<td>&lt;3</td>
<td>73</td>
<td>1.0</td>
<td>187</td>
<td>0.27</td>
<td>17.2</td>
<td>78</td>
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<tr>
<td>SPD213 (391.90 m), Fosterville</td>
<td>3214</td>
<td>27</td>
<td>1012</td>
<td>818</td>
<td>1435</td>
<td>7353</td>
<td>96</td>
<td>244</td>
<td>25.5</td>
<td>651</td>
<td>1.37</td>
<td>52.8</td>
<td>23.15</td>
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<tr>
<td>J1L1A64 Pre-syn-S2 fram and o’growth</td>
<td>152033</td>
<td>1234</td>
<td>1105</td>
<td>1869</td>
<td>1930</td>
<td>3923</td>
<td>142</td>
<td>266</td>
<td>30.6</td>
<td>955</td>
<td>1.31</td>
<td>32.8</td>
<td>2316</td>
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<tr>
<td>J1L1A65 Pre-syn-S2 fram in matrix</td>
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<td>9</td>
<td>660</td>
<td>345</td>
<td>240</td>
<td>4044</td>
<td>106</td>
<td>215</td>
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<td>&lt;0.96</td>
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<td>316</td>
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<td>RHD019 (161.56 m), O’Dwyers pit area, Fosterville</td>
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<td>24</td>
<td>72</td>
<td>613</td>
<td>56</td>
<td>1169</td>
<td>&lt;40</td>
<td>&lt;10</td>
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<td>46</td>
<td>1.22</td>
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<td>136</td>
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<tr>
<td>MY1A11 Pre-early syn-S2 f.g. py</td>
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<td>&lt;1</td>
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<td>&lt;45</td>
<td>19253</td>
<td>&lt;13</td>
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<td>202</td>
<td>&lt;0.45</td>
<td>3.1</td>
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<td>MY1A17 Pre-early syn-S2 gal incl. in py</td>
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<td>2</td>
<td>396</td>
<td>4047</td>
<td>1434</td>
<td>1809</td>
<td>200</td>
<td>&lt;13</td>
<td>2.8</td>
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<td>1.22</td>
<td>&lt;0.2</td>
<td>13101</td>
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<td>RHD019 (161.42 m), O’Dwyers pit area, Fosterville</td>
<td>153871</td>
<td>799</td>
<td>3505</td>
<td>2041</td>
<td>1899</td>
<td>3455</td>
<td>&lt;45</td>
<td>&lt;30</td>
<td>9.5</td>
<td>1199</td>
<td>13.99</td>
<td>20.0</td>
<td>3360</td>
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<tr>
<td>JN2SA5S Syn-S2 fram</td>
<td>2202</td>
<td>11</td>
<td>568</td>
<td>949</td>
<td>60</td>
<td>1466</td>
<td>&lt;20</td>
<td>10</td>
<td>2.5</td>
<td>213</td>
<td>2.35</td>
<td>1.8</td>
<td>825</td>
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</tbody>
</table>

1 Abbreviations used in table: cpy = chalcopyrite, f.g. = fine-grained (for pyrite, typically mixtures of framboidal or framboid-like microcryst aggregates, interspersed with or overgrown by fine-grained euhedral pyrite), fram = framboidal pyrite, gal = galena, mc = marcasite, o’growth = overgrowth, py = pyrite, sph = sphalerite
Upper Mud unit of the Popovich Formation, where it is locally the dominant pyrite type (abundances <2–3 percent, Scott et al., in prep.). It has several common modes of occurrence: (1) sparsely disseminated through the sediment matrix, (2) irregular-shaped and spheroidal polyframboidal clusters (e.g., Love, 1971) clusters, and (3) as minor to major constituents of bedding-parallel lenticular aggregates and laminae of other very fine grained pyrite (Fig. 1). Commonly, all types occur in a single sample. Lenticular aggregates are locally cut by Mississippian bitumen veinlets and are commonly overprinted by soft-sediment slump and compaction features (Fig. 1A), the latter indicating probable formation within

![Figure 1](https://example.com/figure1.png)

**Fig. 1.** Reflected-light photomicrographs of early and late diagenetic framboidal pyrite from the northern Carlin trend, Nevada. A. Bedding-parallel aggregates of very early diagenetic framboidal pyrite overprinted by soft-sediment slump folds and Mississippian(?)-age cleavage. Devonian Popovich Formation, drill hole BSC168c, 853 ft. B. Variation in size and internal morphology of pyrite framboids from same sample as (A). Some framboids are considerably larger than the largest detrital grains (e.g., dashed line at lower left). Note larger framboids have rims and infill of later pyrite. C. Small bioclast almost completely replaced by framboidal pyrite. Basal Upper Mud unit of the Popovich Formation, drill hole GA54c, 1484 ft. D. Detail from (C). Note that the surfaces of the outermost framboids conform to the original shape of the bioclast. E. Framboidal and other fine-grained pyrite concentrated along a late diagenetic stylolitic dissolution seam (S) that cuts a Mississippian bitumen veinlet (V). Rodeo Creek Formation, drill hole CD12c, 852.6 ft. F. Detail from (E).
meters of the sediment-water interface (e.g., Emsbo et al., 1999; Scott et al., in prep.).

Particularly in samples where framboidal pyrite is relatively abundant, there is considerable variation in both the size and internal morphology of the framboids (Fig. 1B). The largest framboids are commonly many times larger than the grain size of the host sediment (Fig. 1B), indicating they did not form in interstitial pore spaces, as assumed in many models of framboidal precipitation. Aggregates of framboidal pyrite also replace organic matter and fossil fragments (Fig. 1C, D), and in such cases, the external morphology of the outermost framboids may conform to the original shape of the replaced fragment. There is commonly partial infilling by later pyrite (Fig. 1B) and/or other sulfides (e.g., sphalerite) of both individual framboids and spheroidal polyframboidal clusters.

Framboidal pyrite of interpreted late diagenetic origin

Very fine grained and framboidal pyrite is also concentrated along stylolitic seams that cut both early bedding-parallel pyrite aggregates and Mississippian bitumen veinlets (Fig. 1E, F). The stylolitic seams developed both parallel and oblique to bedding and may have formed during emplacement of the Roberts Mountains allochthon, continued burial, or later (e.g., Mesozoic) deformation events. Significant differences in the composition (Fig. 2, Table 1) and morphology of pyrite in the stylolites, compared to early-formed pyrite in the surrounding rock, suggest that pyrite enrichment along stylolites is not (primarily) due to the concentration of existing, relatively insoluble phases during stylolite development. However, determining the trace element compositions of fine-grained pyrite is potentially problematic in cases such as this, where analytical volumes exceed the pyrite grain size. Trace elements from the surrounding matrix and inclusions of other phases may contribute significantly to the apparent composition of fine-grained pyrite (Raiswell and Plant, 1980) and in particular framboidal pyrite, where 25 to 90 percent of the framboid volume is composed of material other than pyrite (e.g., Rickard, 1970; Love et al., 1984). Nonetheless, whether or not specific trace elements occur principally in pyrite can be assessed from their correlation with elements that do not occur at significant concentration in pyrite but do in minerals comprising the surrounding matrix (e.g., Al, Si, Mg, and Ca; e.g., Raiswell and Plant, 1980).

The laser ablation ICP-MS analyses of framboidal pyrite in sample CD12c_852.6 ft (e.g., Fig. 3) indicate that variations in the abundance of Pb, Cu, Sb, Co, Mn, Mo, As, Tl, Zn, Ag, and Se generally correlate moderately to strongly with Fe and poorly with Al (phylllosilicates), Mg-Ca (dolomite), and Si (quartz and phyllosilicates). This indicates these elements are either predominantly contained in pyrite or occur in phase(s) that are spatially related, and in constant proportion, to pyrite. Vanadium, on the other hand, is strongly correlated with Al, suggesting it principally resides in clay or mica (Fig. 2A). Thus, apparently higher V concentrations for the stylolite-hosted pyrite simply reflect higher proportions of matrix in these analyses, compared to those for the denser bedding-parallel pyrite aggregates.

Framboidal pyrite of interpreted late hydrothermal origin

Framboidal pyrite also occurs in some late Carlin ore-stage (i.e., Eocene) pyrite-marcasite veins (Fig. 4). Unlike Carlin ore-stage pyrite, which is all extremely fine grained (mostly <1 μm) and primarily developed in the wall rocks with Fe sourced from dissolution of adjacent Fe-bearing minerals (Cline et al., 2005), late ore-stage mineralization displayed greater Fe mobility with the local development of micro-colloform-textured pyrite and/or marcasite veins (Emsbo et al., 2003). Pyrite and/or marcasite precipitated in the late-stage veins is compositionally distinctive, being strongly enriched in As, Sb, and Tl but with lower to much lower levels of the other trace elements generally contained in ore-stage Carlin-type pyrite (e.g., Au, Ag, Cu, Pb; Emsbo et al., 2003).

Fig. 2. Scatter plots showing variations in abundance of (A) V, (B) Se, and (C) Co relative to Al in LA-ICPMS data for early and late diagenetic pyrite from sample CD12c_852.6 ft. Data are quantified assuming all elements are contained in pyrite. For elements primarily contained in other minerals (e.g., inclusions or surrounding matrix), only element ratios are likely to be meaningful. Strong correlation between V and Al suggests the apparently higher V content of pyrite in the stylolites reflects a higher proportion of V-bearing clay or mica in these analyses. Variations in Se and Co are independent of Al and interpreted to reflect differences in pyrite composition.
Homogenization temperatures for fluid inclusions in quartz from late ore-stage veins have a mean of 220°C and a minimum of 175°C (Lamb, 1995; Emsbo et al., 2003). Most Carlin-type deposits are interpreted to have formed between 1- and 3-km depth (Cline et al., 2005), and a similar depth range for the late Carlin ore-stage veins is likely. Isotopic and compositional characteristics suggest that late ore-stage fluids formed by mixing between the Carlin ore fluid and cooler, more oxidized meteoric water during the waning stages of the hydrothermal system (Emsbo et al., 2003).

Laser ablation ICP-MS analyses indicate that both framboids and colloform-textured marcasite in a late ore-stage vein from the Gold Quarry mine (sample QRC1750_22 ft, Fig. 4, Table 1) are highly enriched in arsenic (2.9–12.0%), antimony (0.4–1.9%), and thallium (176–4,280 ppm). While the spatial resolution of the laser does not permit clear compositional discrimination of the framboids and the enveloping marcasite, analyses centered on framboids suggest these are preferentially slightly enriched in gold (i.e., 0.5–1.5 ppm Au), consistent with the interpreted late Carlin ore-stage timing (e.g., Emsbo et al., 2003). Framboidal pyrite in sample QRC1750_22 ft is restricted to veins or immediately adjacent halos of intensely sulfidized wall rock and is always overgrown by the earliest stage of microcolloform textured marcasite. The framboids exhibit the same range in size and microcrystal shape, size, and packing arrangement as those interpreted to be of early diagenetic origin (cf. Figs. 1B, 4B).

Framboidal Pyrite from Lower Paleozoic Turbidites, Fosterville, Central Victoria

Framboidal pyrite is minor (<<1%) but widespread in the tightly folded Lancefieldian (i.e., lowermost Ordovician) deep marine turbidites that host the >3 Moz Au (Hitchman et al., 2008) Fosterville gold deposit, central Victoria, Australia (Fig. 3). Framboidal and fine-grained pyrite in stylolites (delineated by white dashed lines) truncating a Mississippian bitumen veinlet (V), Rodeo Creek Formation, drill hole CD12c, 832.6 ft. Yellow circle denotes location of LA-ICPMS analysis shown in (B). B. Plot showing variations in count-rate for selected trace elements during analysis of the small framboidal pyrite cluster shown in (A). The laser was turned on at 32 s and burned through the framboid cluster after 20 s (reflected by an abrupt decrease in signal for Fe and increase for Al). Variations in count-rate (proportional to abundance) for the other elements shown reflect proportion of Fe, rather than elements concentrated in the surrounding matrix (e.g., Al). See text for further discussion.

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The succession is part of the Lower to Middle Ordovician Castlemaine Group, which hosts numerous small to large gold deposits in the Bendigo zone (Fig. 5A). Most deposits in this region formed at ca. 440 Ma, during the waning stages of fold and cleavage development in the Late Ordovician–Early Silurian Benambran orogeny (Arne et al., 1998; Foster et al., 1998; Willman, 2007), and contain predominantly fault- and vein-hosted free gold (Cox et al., 1995; Schaub and Wilson, 2002). In contrast, the Fosterville deposits (1) are Devonian (e.g., mineralized felsic dikes with zircon U-Pb ages ranging

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**Fig. 5.** A. Distribution of major structural zones in Victoria (after Vandenberg et al., 2000). Location of Fosterville is indicated in the eastern part of the Bendigo zone. B. Simplified map of the Fosterville goldfield, showing the distribution of deposits and drill holes logged and sampled for this study. C. Cross sections for drill holes RHD019 and GT8, based on first author's and Fosterville mine data. Locations of Devonian mineralized zones and samples (from these drill holes) described in this study are indicated.
from 394 ± 17 to 371 ± 6 Ma: Arne et al., 1998; Bierlein et al., 2001a), (2) formed during reverse-sinistral reactivation of the earlier Fosterville and O’Dwyers fault zones (Fig. 5; Wang and White, 1993; Leader et al., 2010), and (3) contain refractory gold in disseminated, wall-rock–hosted fine-grained arseniopyrite and arsenian pyrite; Zurkic, 1998; Mernagh, 2001; Bierlein et al., 2000, 2004). The host rocks at Fosterville were metamorphosed to anchizonal grade (prehnite-pumpellyite facies) during the Benambran orogeny and progressively exhumed during the Devonian (Offler et al., 1998).

Framboidal pyrite distribution at Fosterville

Framboidal pyrite is rare in the ore zones at Fosterville but ubiquitous in surrounding shales and siltstones. However, it only occurs in high enough concentrations to be visible to the naked eye in the wall rocks adjacent to laminated, bedding-parallel, quartz-carbonate shear veins (Fig. 6) and locally in wall-rock fragments in the veins themselves. Here framboidal pyrite is generally associated with disseminated or nodular aggregates (Fig. 6A, C) of coarser grained subhedral to euhedral pyrite (and rarely, marcasite) and locally trace amounts of fine-grained chalcopyrite, sphalerite, and galena. Sulfide contents rarely exceed a few percent and decrease abruptly within a few, to a few tens of centimeters of the veins. Rarely, pyrite nodules and bedding-parallel bands of fine-grained and framboidal pyrite occur up to several meters from the veins. Based on morphology, much of this pyrite has previously been interpreted as sedimentary or diagenetic in origin (e.g., Bierlein et al., 2004) and some clearly predates development of the axial planar cleavage (e.g., Figs. 6, 7). However, the apparent restriction of significant sulfide development to either major fault zones (e.g., Fosterville fault, Fig. 5B, C) or the wall rocks within several meters of bedding-parallel shear veins (Fig. 6), suggests it formed during later, structurally controlled hydrothermal fluid flow.

Laminated bedding-parallel shear veins are common features of the Castlemaine Group and interpreted to have formed during folding as a result of localized flexural slip in thick incompetent beds or at interfaces between beds of different rheology (Jessell et al., 1994; Fowler, 1996; Fowler and Windsor, 1997). Larger veins generally occur in thicker shale, slate, or siltstone units, commonly within 10 cm of overlying sandstone beds (Jessell et al., 1994; Cox et al., 1995; Fowler, 1996; Boucher et al., 2008). Stratigraphic separation of the bedding-parallel veins at Fosterville ranges from 1 to 20 m, and is similar to other goldfields in the Bendigo zone (e.g., Jessell et al., 1994; Fowler and Windsor, 1997).

Many of the veins continue around fold hinges without significant changes in thickness, suggesting they formed early during folding (Willman and Wilkinson, 1992; Jessell et al., 1994; Willman, 2007); however, most clearly postdate initial axial planar cleavage development (Fowler, 1996). At Fosterville, overprinting relationships indicate that major
movement on the veins predated Devonian gold mineralization (Wang and White, 1993), and many (particularly in the hanging wall of the Fosterville fault zone) were not obviously reactivated during that event.

**Sulfide paragenesis and microstructural relationships**

All but one of the samples discussed here are from positions <2 m (distances measured perpendicular to bedding) from bedding-parallel shear veins. Four main spatial and/or microstructural associations of frambooidal pyrite are recognized: (1) minor, scattered individual frambooids in shales, siltstones, and some sandstones; (2) concentrations around and overgrown by pyrite nodules; (3) discontinuous trails and elongate aggregates parallel to bedding and a cryptic, fine-grained mica foliation (S1); and (4) concentrations along the axial planar cleavage (S2). Frambooids of association (1) are generally of ambiguous or indeterminate timing and are mostly too small (<10 µm diam) and sparsely disseminated to be meaningfully analyzed by LA-ICPMS. As a result they are not considered further here.

**Pre- to early synclineage frambooidal pyrite:** Frambooidal pyrite is concentrated around the margins of many dense (nodular) aggregates of fine-grained anhedral to euhedral pyrite. Nodules primarily occur in shales and silty shales, generally within 1 m of bedding-parallel shear veins (Fig. 6A, C). They are irregular to ovoid in shape and up to 3 cm in maximum dimension. Commonly at their peripheries (and less commonly through their interiors) well-preserved frambooids are evident in the cores of some euhedral pyrite grains (Fig. 7B), indicating the coarser grained largely postdates the frambooidal pyrite (e.g., Rickard and Zweifel, 1975; Raiswell and Plant, 1980). The extent to which frambooidal pyrite also recrystallized to form the later pyrite (e.g., Large et al., 2007) is not clear.
Well-developed quartz-filled strain fringes and variations in both the intensity and orientation of S2 around the nodule margins indicate that most formed very early during or before development of the axial planar cleavage (Fig. 7A). In contrast (although partly obscured by S2), the cryptic, fine-grained, bedding-parallel mica foliation (S1), which appears to represent the main episode of metamorphic mica growth in these rocks, is generally of similar intensity and orientation around the nodules, suggesting they may overgrow this fabric.

Most framboidal pyrite at Fosterville occurs in thin, discontinuous trails or elongate densely clustered aggregates aligned parallel to bedding and S1 (i.e., association (3) above). In the best developed example (sample SPD213_351.90 m), a 3-mm-wide bedding-parallel band of densely clustered framboidal pyrite spans the entire 4.7-cm width of the drill core (Fig. 6B, D). This band occurs at the outer margin of a 30-cm halo of fine-grained disseminated sulfides developed in the hanging wall of a 7-cm-wide laminated bedding-parallel shear vein (Fig. 6B). More commonly, however, framboid aggregates are up to several millimeters long and <200 \( \mu \)m wide (Fig. 8) or form spheroidal clusters up to 200 \( \mu \)m in diameter. Some are mixtures of true framboidal pyrite (e.g., Ohfuji and Rickard, 2005) and irregular clusters of pyrite microcrystals. Overgrowths of later, coarser grained pyrite are relatively common (Figs. 7C, 9B-D), with some partial framboid cluster infilling or replacement by chalcopyrite, sphalerite, and galena (Figs. 8, 9B, C).

The S1 parallel framboidal pyrite aggregates (and commonly overgrowths of coarser grained pyrite) are overprinted by S2, indicating they formed during or prior to the earliest stages of cleavage development. Their timing with respect to S1 is more equivocal. Many framboid aggregates have small quartz- or mica-filled strain fringes recording S2 parallel extension along their edges (Fig. 8A) but no similar features recording S1 parallel extension have been observed, even where S1 is strongly developed.

Syn- to postcleavage framboidal pyrite: Abundant pyrite framboids, <10 \( \mu \)m in diameter, occur in a discontinuous thin band along the hanging-wall contact of a reactivated bedding-parallel quartz-carbonate vein in sample RHD019_161.42 (i.e., dark material indicated by white arrow in Fig. 9A). The framboidal pyrite principally occurs in domains of well-developed S2 and is largely absent from the intervening microlithons (Fig. 9E, F). This distribution suggests the framboids mostly formed during or after S2. Furthermore, numerous ovoid to lenticular aggregates of pyrite microcrystals within the S2 domains are aligned parallel to the cleavage (Fig. 9G). The size, shape, and orientation of these aggregates suggest they may be flattened, originally spheroidal framboids. If so, differences in the amount of flattening may indicate protracted framboid nucleation during cleavage development.

In sample GT8_94.4 m (see Fig. 5C for location), sulfide distributions and overprinting relationships suggest that both pre- (to early syn-) S2 and late syn-S2 framboidal pyrite occur in a 1.5-cm-thick shale layer containing very thin, bedding-parallel shear veins (Figs. 10, 11). Most of the framboidal pyrite occurs in thin, relatively continuous, bedding and/or S1 parallel bands and laminae that are clearly offset by S2 (Fig. 11). Denser clusters are typically overgrown by coarser grained euhedral pyrite (and lesser marcasite) that also largely predates the cleavage. However, framboidal pyrite that is less commonly overgrown by euhedral pyrite is also concentrated along S2 (Figs. 10C-D, 11). This could be due to concentration of existing, relatively insoluble minerals along cleavage domains (e.g., Gray, 1979; Gray and Durney, 1979), however later sulfide development along S2 is also suggested by the apparent restriction of minute galena grains to these domains (Fig. 10C), as well as a slight increase in the grain size of S1 parallel pyrite lamellae where reoriented along S2 (Fig. 11).

**Volume loss from S2 cleavage domains at Fosterville**

Previous studies in the central Victorian goldfields indicate that Ti was essentially immobile during deformation and hydrothermal alteration (e.g., Glasson and Keays, 1978; Gao and Kwak, 1997). Thus to determine whether pyrite concentrations along S2 in sample GT8_94.4 m reflect the concentration of relatively insoluble phases by dissolution, volume loss from the cleavage domains was estimated by comparing their Ti contents to those of the adjacent microlithons. Element variations along eight adjacent LA-ICPMS line analyses for a 240- \( \times \) 500-\( \mu \)m area of relatively low pyrite density in
FIG. 9. A. Bedding-parallel quartz-carbonate shear vein in thinly bedded shale, siltstone, and sandstone. Fosterville drill hole RHD019, 161.27–161.6 m (see Fig. 5C for location). Bedding (S₀) and the axial planar cleavage (S₂) indicated by the solid and dashed lines, respectively. Thin white line to the left of the vein marks the edge of a sandstone dike, possibly rooted into the sandstone bed (sst) ~10 cm below the vein. Black and white arrows denote the locations of samples RHD019_161.56 m and 61.42 m, illustrated in parts (B)-(D) and (E)-(G), respectively. B. Reflected-light photomicrograph of fine-grained euhedral pyrite (py) overgrowths on elongate bedding-parallel aggregate of framboidal pyrite. Framboidal pyrite in the cores of these grains is extensively replaced by galena (gal) and chalcopyrite (cpy). C. Detail from (B). D. Reflected-light photomicrograph showing oscillatory zoning in euhedral pyrite that overgrows a small cluster of framboidal pyrite and galena. Zoning is highlighted by variations in degree of natural tarnish. E. and F. Plane-polarized and reflected-light photomicrographs showing detail from discontinuous dark band (indicated by white arrow in A) at the hanging-wall contact of the shear vein. Framboidal pyrite is well developed in the S₂ cleavage domains but largely absent from the intervening microlithons (m) where the bedding-parallel foliation S₁ is preserved. G. Reflected-light photomicrograph of cleavage domain. Ovoid to lenticular aggregates of pyrite microcrystals aligned with S₂ are interpreted as flattened originally spheroidal framboids. Small grains of graphite (gph) are also aligned with S₂.
the shale were determined (Fig. 12). Element maps on the left in Figure 12 show the total variation in counts for each isotope, whereas maps on the right show the ratio of counts for each isotope divided by counts for $^{49}$Ti. Except for a few small zircon(?) crystals (small bright spots in Zr/Ti map), there is little variation in the Ti/Zr ratio across the analyzed area, suggesting both elements were essentially immobile during cleavage formation, at least on scales larger than a few tens of microns (see also Glasson and Keays, 1978).

On average, Ti concentrations along $S_2$ are $2.7 \times$ higher than those in the adjacent microlithons (Fig. 12), equating to a volume loss of 63 percent from the cleavage domains (Fig. 13). Overall volume loss is <20 percent considering $S_2$ domains comprise <30 percent of the shale. This estimate is similar to that of Glasson and Keays (1978), who determined ca. 50 percent volume reduction from cleavage domains in similarly deformed strata at the western margin of the Bendigo zone. Magnesium, Mn, Si, Al, and Fe are all depleted from the cleavage domains, suggesting a breakdown of phyllosilicates ($\pm$Fe oxides?) during cleavage development, liberating Ti and Fe for the development of rutile and pyrite, respectively. In contrast, normally mobile elements such as Sb, As, Ag, Au, Mo, and Pb are concentrated (most likely in pyrite or other sulfides) along the $S_2$ domains. The relatively high Pb/Ti ratio of the $S_2$ domains suggests the addition of externally sourced Pb, consistent with the apparent restriction of galena to these domains (e.g., Fig. 10C).

Trace element composition of framboidal pyrite at Fosterville

Trace element compositions of framboidal pyrite in the Fosterville samples were determined by LA-ICPMS (Table 1). Scatter plots for selected trace elements are shown in Figure 14. For comparison, compositional data for two pre-$S_2$ pyrite nodules (samples GTS_23.2 m and DALD017_66.28) are also provided (Table 1, Fig. 14). Notwithstanding the problems in obtaining truly representative trace element data for very fine grained pyrite (see previous), patterns in laser ablation data similar to those illustrated in Figure 3 indicate...
that (except for Al, V, Th, and U) elements listed in Table 1 generally vary sympathetically with Fe, suggesting their inclusion in pyrite, or show maximum concentrations coincident with higher proportions of pyrite, suggesting they reside in either coprecipitated, infill, or replacive phases.

The results indicate considerable variation in the trace element content of the framboidal pyrite, although it is generally more enriched than spatially related pyrite nodules and disseminated fine-grained euhedral pyrite (see also Raiswell and Plant, 1980; Large et al., 2007). Syn- to late-S2 framboidal pyrite in sample RHD019_161.42 m is significantly more enriched in Au, As, Sb, Ni, and Co than that formed prior to the early stages of cleavage development (including that in sample RHD019_161.56 m, <20 cm away; Fig. 14, Table 1). Unfortunately, in the only sample clearly containing both pre- and syn-S2 framboidal pyrite (sample GT8.94.4 m), the younger framboids are all too small and sparsely distributed along S2 to permit meaningful compositional analyses by LA-ICPMS.

**Pb isotope composition of early-formed sulfides at Fosterville**

Meffre et al. (2008) and Woodhead et al. (2009) show that the Pb isotope systematics of pyrite containing several tens to several thousands of ppm Pb (e.g., most preore-stage pyrite at Fosterville) can be effectively characterized by LA-ICPMS, providing additional constraints on age and crystallization sequence. However, in situ Pb isotope analysis of very fine grained pyrite is potentially problematic due to Pb contributions from the surrounding matrix (Meffre et al., 2008). Owing to the relatively large laser beam diameters used for the Pb isotope analyses, matrix typically constitutes a high proportion (i.e., >50%) of the material analyzed, even for relatively dense aggregates of framboidal pyrite. Thus to help evaluate the influence of matrix Pb in such cases, the Pb content and isotopic composition of the matrix in two framboidal-rich samples (RHD019_161.42 m and SPD213_351.90 m) were also determined.

The Pb contents and isotopic compositions of framboidal pyrite in sample RHD019_161.56 m could not be directly

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![Figure 11](https://example.com/figure11.png)

**Fig. 11.** Pyrite distribution (black spots) across part of the shale layer illustrated in Figure 10A. Image produced from stitched mosaic of twenty-five 2 × 1.5-mm (5x) reflected-light photomicrographs delineating grains down to ca. 5-µm diam. Threshold levels were adjusted so that only the most highly reflective phases (predominantly pyrite) were visible. To enhance visibility at the scale of reproduction used here, 2-pixel-wide layer added to all reflective grains. Although it was not possible to exclude all grains other than pyrite by the threshold method used (and still retain visibility of most pyrite), crosschecking against the thin section indicates that the figure accurately reflects the pyrite distribution. While most pyrite largely predates S2, additional pyrite growth during cleavage development is indicated by anomalous concentrations of pyrite along the cleavage and a slight coarsening of earlier S1 parallel pyrite aggregates where realigned parallel to S2.
determined due to common infill and replacement by galena. Nonetheless, the Pb isotope composition of the galena (determined by solution ICPMS, see “Methods”) constrains the minimum age of framboid formation in this sample. Pb isotope data was also obtained for two pre-S2 pyrite nodules (samples DALD017_66.28 m and GT8_23.2 m) that overgrow (or replace) earlier clusters of framboidal pyrite (e.g., Fig. 7B).

Weighted mean Pb isotope ratios for the sulfides are summarized on conventional 207Pb/204Pb-206Pb/204Pb diagrams in Figure 15. Results are summarized in Table 2 (for tabulation of all results see electronic attachment). Similar results for pre-S2 pyrite nodules in samples DALD017_66.28 m and GT8_23.2 m were obtained using both the quadrupole and MC instruments, although only the more precise MC-ICPMS data are plotted in Figure 15. Data for these samples and the galena in sample RHD019_161.56 m all plot on the 450 Ma crust-mantle mixing isochron for the eastern Lachlan orogen (Carr et al., 1995), close to the crustal end-member composition (Fig. 15A). Lead in framboidal pyrite in samples

Fig. 12. Laser ablation ICP-MS maps showing variations in element abundance in part of the shale layer illustrated in Figure 10A, compiled from eight adjacent 30 × 540-µm line scans with ca. 160 readings per line. The map covers several microthlons and cleavage domains in an area of relatively low pyrite density, away from obvious S0 and S1 parallel pyrite-rich lamellae. Maps on left show total variation in counts for each isotope (rolling average of three readings), whereas maps on the right show counts for each isotope divided by those for 49Ti (assumed immobile). Magnesium, Si, Al, and Fe are moderately to significantly depleted, relative to Ti, along S2 domains, whereas Sb, As, Ag, Au, Pb, and Ag, Mo (not shown) are slightly to significantly enriched.

Fig. 13. Total volume loss from cleavage domains can not be determined from the final geometry of fabric elements. This cartoon shows two different deformation paths that produce the same final geometry of fabric elements. Greater volume loss from cleavage domains in the upper example reflects the earlier onset of localized dissolution during microfolding.
RHD019_161.42 m (syn- to post-S2) and SPD213_351.90 m (pre- to early syn-S2) is more radiogenic but also plots close to the crustal Pb curve (Fig. 15). Both the quadrupole and MC data show a greater spread in \(^{206}\text{Pb}/^{204}\text{Pb}\) ratios for framboid-rich aggregates than for the pyrite nodules (Fig. 16), suggesting matrix Pb contribution may be more significant for the framboidal pyrite.

Matrix contributions to pyrite Pb isotope compositions: For the quadrupole instrument data, the relative proportions of (framboidal) pyrite and matrix analyzed were estimated from the measured Al/Fe ratios. This indicates matrix typically constitutes 50 to 80 percent of the material ablated (see Appendix), consistent with visual estimates. Because it represents such a high proportion of the material analyzed, the Pb content and isotopic composition of the matrix must be determined in order to evaluate its likely impact on the apparent Pb isotope composition of the framboidal pyrite.

Fig. 14. Scatter plots of selected LA-ICPMS trace element data for framboidal and other early-formed pyrite at Fosterville. A. Au vs. Pb. B. Ag vs. Sb. C. Co vs. Ni. See (C) for key to symbols. Although from beds less than 15 cm apart, framboidal pyrite in samples RHD019_161.42 m and RHD019_161.56 m have very different trace element compositions. The interpreted syn-S2 framboids in sample RHD019_161.42 m are more strongly enriched in Au, Sb, Ni, and Co than those formed prior to S2 in sample RHD019_161.56 m. The high Pb contents of framboidal pyrite aggregates in samples GT8_49.4 m and RHD019_161.56 m are due to later overgrowths and replacement by galena.

Fig. 15. A. Conventional \(^{207}\text{Pb}/^{204}\text{Pb}\) vs. \(^{206}\text{Pb}/^{204}\text{Pb}\) plot showing range in Pb isotope composition for pre- to syn-S2 sulfides at Fosterville. A. Pre- or early syn-S2 galena (solution ICPMS, sample RHD019_161.56 m). B. Syn-S2 framboidal pyrite (LA Quad-ICPMS, sample RHD019_161.42 m). C. Pre- or early syn-S2 framboidal pyrite (LA Quad-ICPMS, sample SPD213_351.90 m). D. and E. Pre-S2 pyrite nodules (LA MC-ICPMS, samples DALD017_66.28 m and GT8_23.2 m). Thick dashed lines are crust and mantle Pb evolution curves and thin dashed lines are mixing isochrons for the eastern Lachlan orogen after Carr et al. (1995). Lead crustal growth curve of Stacey and Kramers (1975) shown in gray. B. As for (A) but with 450 Ma U correction applied to quadrupole LA-ICPMS Pb isotope data for framboidal pyrite samples (B) and (C). U corrections to MC ICPMS data for pre-S2 pyrite nodules (D) and (E) are likely to be negligible based on quadrupole LA ICPMS data for these samples (Table 2). Range in initial Pb isotope ratios for reef-hosted sulfides from Ballarat and Bendigo goldfields (Andrew et al., 2002) shown for comparison.
Quadrupole LA-ICPMS analyses of the matrix, in areas largely or entirely devoid of pyrite in samples RHD019_161.42 m and SPD213_351.90 m yield imprecise but highly radiogenic Pb isotope compositions (Fig. 16). Even when analyzed with the maximum beam diameter (i.e., 110 µm), Pb counts for the matrix were below the optimum range for isotopic characterization on this instrument, suggesting Pb contents <100 ppm (e.g., Meffre et al., 2008). Whole-rock geochemical data indicate carbonaceous and sericitic layers in the sequence adjacent to sample SPD213_351.90 m contain ca. 30 and 50 ppm Pb, respectively (Table 3). Although neither the Pb content nor isotopic composition of the matrix in these samples is particularly well constrained, modeling data for sample RHD019_161.42 m based on best estimates of these parameters suggests matrix-derived Pb only contributes significantly to the measured Pb isotope composition for two analyses in which framboidal pyrite constitutes <10 percent of the ablated material (see Appendix, Table 4).

Lead isotope data for sample SPD213_351.90 m was predominantly obtained from dense clusters of framboidal pyrite overgrown by euhedral pyrite (e.g., Fig. 7C). Aluminum to Fe ratios for these analyses indicate that nonpyritic matrix constitutes <14 percent of the analyzed material (Table 4C) and is unlikely to contribute significantly to the measured Pb isotope compositions. Data for a densely clustered framboid aggregate lacking euhedral pyrite overgrowths (i.e., analysis AU29E09, ~44% nonpyritic matrix, see Table 4C) are indistinguishable from that for aggregates overgrown by euhedral pyrite, suggesting the overgrowths are either of similar Pb isotope composition or do not contribute significantly to the measured values.

Uranium corrections for quadrupole LA-ICPMS data: The quadrupole LA-ICPMS data were also corrected for Pb produced by radioactive decay in U-, Th-bearing mineral inclusions (e.g., Meffre et al., 2008, see Appendix). Assuming a maximum pyrite crystallization age of 450 Ma shifts the Pb isotope composition of framboidal pyrite in sample RHD019_161.42 m to slightly less radiogenic values but makes negligible difference to results for pyrite in the other samples (Fig. 15B, Table 2). It is not possible to correct the MC-ICPMS data because the instrument configuration used for this study does not allow for the simultaneous measurement of U, Th, and Pb.

Discussion

Concentrations of framboidal pyrite along (1) posthydrocarbon generation stylolites and (2) later hydrothermal veins in Upper Devonian sedimentary rocks of the northern Carlin trend, as well as (3) in narrow sulfidic halos to bedding-parallel shear veins in Lower Ordovician turbidites at Fosterville, central Victoria, indicate that framboid formation is not restricted to surficial environments and may occur, in favorable microniches, over a considerable depth range in the upper crust. The similarity in the size and internal morphology of framboids formed in various settings suggests controls on framboid development may be common to all settings.

Framboidal pyrite concentrations along dissolution surfaces, such as stylolites and cleavages, may be explained either by preferential crystalization along these surfaces or the concentration of existing, relatively insoluble minerals as
dissolution proceeds (Gray, 1979; Gray and Durney, 1979). The latter process clearly accounts for some pyrite enrichment along S2 at Fosterville (e.g., Fig. 11). However, although significant, the ca. 60 percent volume loss estimated for S2 domains in sample GT8_94.4 m only accounts for a ~3\times increase in the amount of pyrite along the cleavage, compared to adjacent microlithons. In this sample, sulfide and particularly framboidal pyrite concentrations along S2, may exceed those of the microlithons by a factor of ten or more (e.g., Figs. 10C, 11), implying that much of the sulfide precipitated during or after cleavage development. Trace element and Pb isotope compositional differences between framboids with distinct microstructural associations at Fosterville also support precipitation at different times from fluids of different composition (Figs. 14, 15).

Microstructural constraints on framboid formation

Widespread overprinting by soft-sediment slump and differential compaction features indicate that most framboidal pyrite in the upper Popovich Formation on the northern Carlin trend probably formed during sedimentation or shallow-level diagenesis (e.g., Scott et al., in prep.; this study). At Fosterville, however, the intensity of grain-scale deformation generally precludes the recognition of similar features (if originally present), and the timing of initial framboid development is more equivocal. Cleavage overprinting relationships indicate most formed either early during or before development of S2 (e.g., Figs. 7, 8, 11) and thus no later than the earliest stages of regional folding. However, this does not necessarily imply a syngenetic or early diagenetic origin.

Overprinting relationships between framboidal and other early-formed sulfides and the bedding-parallel mica fabric (S1) at Fosterville are partly obscured by later cleavage development. However, in general, there appears to be little change in either S1 intensity or orientation in the matrix around either pre-S2 pyrite nodules or the larger aggregates of framboidal pyrite, nor are S1 parallel strain fringes developed at their margins. Even where S1 is strongly developed

![Graph](image)

**Fig. 16.** $^{207}$Pb/$^{204}$Pb vs. $^{206}$Pb/$^{204}$Pb plot showing quadrupole and MC LA-ICPMS data (1σ error ellipses) for framboidal pyrite in sample RHD019_161.42 m. The large spread in $^{206}$Pb/$^{204}$Pb ratios is interpreted to reflect variations proportions of more radiogenic matrix Pb in the analyses. The approximate Pb isotope compositions of the shale matrix in this sample (vertical hatch) and in sample SPD213_351.90 m (horizontal hatch) were used to assess the likely influence of matrix Pb on the apparent Pb isotope compositions of the pyrite (see Appendix).

<table>
<thead>
<tr>
<th>TABLE 3. Whole-Rock and LA-ICPMS Constraints on Matrix Composition</th>
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<td><strong>Whole-rock data</strong></td>
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<td>U (ppm)</td>
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<td>Integration interval</td>
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<tr>
<td>Integration interval</td>
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<td>47–77 s (AU29C07)</td>
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</table>

Notes: LA-ICPMS data quantified assuming Al concentrations equal to those in sample SPD213_352-32: carbonaceous layer (*) and sericitic layer (†)
### Table 4. Matrix Pb Corrections to Pb Isotope Determinations for Framboidal Pyrite

#### A. Sample number RHD019 (161.42 m), Model 1, matrix Pb isotope composition: $^{206}\text{Pb}^{204}\text{Pb} = 19.42,^{207}\text{Pb}^{204}\text{Pb} = 15.73,^{208}\text{Pb}^{204}\text{Pb} = 38.42$

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<th>Matrix proportion</th>
<th>Measured ratios</th>
<th>Recalculated pyrite Pb isotope ratios</th>
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</table>

#### B. Sample number RHD019 (161.42 m), Model 2, matrix Pb isotope composition: $^{206}\text{Pb}^{204}\text{Pb} = 19.94,^{207}\text{Pb}^{204}\text{Pb} = 15.24,^{208}\text{Pb}^{204}\text{Pb} = 39.00$

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<th>Matrix proportion</th>
<th>Measured ratios</th>
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framboidal pyrite aggregates are not obviously disaggregated, or flattened due to S1 parallel extension, as is locally observed for framboidal pyrite aggregates overprinted by S2 (e.g., Figs. 8, 9G). This suggests that the framboidal aggregates developed along existing fabric planes; perhaps as a result of similar processes to those inferred to account for framboid development along S2 (see below). Collectively, microstructural relationships and the apparent restriction of well-developed framboidal pyrite aggregates to sulfidic halos around bedding-parallel shear veins, strongly suggest they are genetically related. Most, if not all, significant early sulfide development at Fosterville appears to reflect the episodic discharge of hydrothermal fluids along bedding-parallel slip surfaces formed during folding.

**Pb isotope constraints on framboid formation at Fosterville**

Previous Pb isotope studies in southeastern Australia provide a basis for evaluating the temporal significance of sulfide Pb isotope data from Fosterville. In the eastern Lachlan orogen, the Pb isotope systematics of Ordovician to Carboniferous mineral deposits are consistent with Pb derivation from either mantle or long-lived crustal reservoirs, or from a mixture of both sources (Carr et al., 1995). While some large-scale heterogeneity in Pb reservoirs across the orogen appears likely, Andrew et al. (2002) found that Pb isotope systematics (and model ages) for sulfides from central and western Victorian gold deposits (western Lachlan orogen) were broadly consistent with the Carr et al. (1995) model.

The 450 to 400 Ma Pb model ages for sulfides formed prior to Early to Middle Devonian gold mineralization at Fosterville (Fig. 15) support their interpreted epigenetic origins. While only broadly indicative of crystallization ages, these Pb model ages overlap with established deformation and mineralization ages in central Victoria (Foster et al., 1998; Foster and Gray, 2000; Vandenberg et al., 2000). The Pb isotope compositions of pre- to early syn-S2 pyrite nodules (samples DALD017_66.28 m and GT8_23.2 m) and galena (sample RHD019_161.56 m) at Fosterville overlap with the least radiogenic Pb isotope compositions for sulfides from auriferous reefs at Bendigo, 30 km to the west (Fig. 15B, e.g., Bierlein and McNaughton, 1998; Andrew et al., 2002). However, whereas major gold mineralization at Bendigo occurred during the late stages of local fold and cleavage development (ca. 440 Ma, Foster et al., 1998; Arne et al., 2001; Schaubs and Wilson, 2002; Willman, 2007), sulfides with similar Pb isotope compositions at Fosterville formed much earlier during the local fold development. In contrast, syn-S2 framboidal pyrite at Fosterville (sample RHD019_161.42 m) yielded a distinctly younger Pb model age. Collectively, this data support the previously postulated eastward progression of fold and cleavage development across the Bendigo zone (e.g., Foster et al., 1998; Foster and Gray, 2000).

Not all the Fosterville Pb isotope data are consistent with relative timings based on cleavage overprinting relationships, however. Framboidal pyrite in sample SPD213_351.90 m yielded the most radiogenic (weighted average) Pb isotope composition of any of the samples considered here (Fig. 15, Table 2), yet cleavage overprinting relationships suggest it formed no later than the early stages of S2 development; before framboidal pyrite in sample RHD019_161.42 m. This
discrepancy implies that at least some of the Pb in pyrite from sample SPD213_351.90 m may have been derived from a distinct reservoir that did not evolve along the same growth curve as the dominant source of Pb in pyrite from the other samples.

Implications for frambooidal formation mechanisms

This paper primarily addresses the where and when of frambooidal formation, rather than how and why. Nonetheless, relationships documented here do have implications for the processes by which frambooidal pyrite forms. In particular, no obvious morphological differences were recognized between frambooidal pyrite of syngenetic-early diagenetic origin, and that interpreted have formed during later burial, deformation or hydrothermal alteration. This suggests that crystallization paths were either independent of the geologic environment in which the frambooids formed or that different crystallization paths produce a similar range in frambooidal morphologies.

Ideas about the formation of frambooidal pyrite have changed considerably over the last 50 years. Prior to the 1970s, biogenic processes were widely considered critical (Schneiderhöhn, 1923; Love, 1957; Love and Zimmerman, 1961; Rickard, 1970). Subsequent experimental syntheses of frambooidal pyrite demonstrated this is not the case (e.g., Berner, 1969; Sweeney and Kaplan, 1973; Wilkin and Barnes, 1996; Butler and Rickard, 2000). However, much of the experimental work (see Ohfuji and Rickard, 2005, for a review) was interpreted to indicate frambooidal formation involves complex crystallization paths, and the critical role of specific precursors, most notably the magnetic thiospinel, greigite (Fe₃S₄, e.g., Sweeney and Kaplan, 1973; Wilkin and Barnes, 1997). Later experimental work by Butler and Rickard (2000) indicated greigite is also not required and that frambooidal pyrite can form directly via the dissolution of solid FeS and subsequent rapid oxidation of the resultant FeS₄(aq) cluster complexes by aqueous H₂S.

The attainment of very high pyrite supersaturations appears to be critical for the formation of frambooidal pyrite (Butler and Rickard, 2000; Ohfuji and Rickard, 2005). The small size, large number (up to 10⁶), and uniform morphology of the microcrystals comprising individual frambooids suggest nucleation was very rapid, consistent with precipitation from supersaturated solutions (Wilkin and Barnes, 1997; Butler and Rickard, 2000; Ohfuji and Rickard, 2005). Growth of microcrystals is presumably also rapid but limited by nutrient supply. In other words, initially highly supersaturated fluids become undersaturated, with respect to pyrite, as nutrients are depleted by microcrystal growth (Ohfuji and Rickard, 2005).

Rapid oxidation of FeS₄(aq) by H₂S proposed by Butler and Rickard (2000) provides a mechanism for frambooidal formation in relatively reduced or anoxic environments where S²⁻ is by far the dominant sulfur species. As the reactants are dissolved, they also accounts for direct precipitation of frambooidal pyrite from pore waters and hydrothermal fluids (e.g., Chen, 1978; Pichler et al., 1999; this study). Experimental work by Butler and Rickard (2000) and studies of frambooidal distribution in euxinic basins (e.g., Wilkin et al., 1996, 1997) indicate precipitation of frambooidal pyrite is favored by comparatively oxidized conditions close to the SO₄²⁻/S²⁻ “redox” boundary (Ohfuji and Rickard, 2005). Pyrite solubility changes abruptly at this boundary, facilitating development of more highly FeS₂ supersaturated fluids than in reduced (lower Eh) systems with the same total concentrations of Fe and S (Butler and Rickard, 2000; Ohfuji and Rickard, 2005).

Butler and Rickard (2000) also predicted that frambooidal formation may be favored by lower pH conditions, consistent with the intimate association of frambooidal pyrite and colloform-textured marcasite in some hydrothermal precipitates (e.g., Fig. 4; Schouten, 1946; Pichler et al., 1999; this study). Marcasite crystallization is interpreted to be indicative of lower pH conditions (i.e., pH <5, Murowchick and Barnes, 1986; Murowchick, 1992).

Due to the finite rates of mineral dissolution, frambooidal pyrite is unlikely to form via direct replacement of crystalline materials (Rickard, 1970; Butler and Rickard, 2000). Nonetheless, textural relationships in many of the samples considered here suggest that frambooids formed via the partial or selective replacement of their immediate substrate (e.g., Fig. 1B-D). Rickard (1970) suggested such conflicts between textural relationships and inferred crystallization mechanisms could be reconciled if the frambooids formed via the rapid pyritization of amorphous organic matter (including spherical organic globules, as modeled by Raiswell et al., 1993) or (H₂S-filled?) vacuoles in the sediment, where the external morphology of the frambooids (or frambooid aggregates) is partly or entirely controlled by the shape of the precursor.

The requirement of high FeS₂ supersaturations has important hydrological implications for frambooidal crystallization, as migration of such fluids over geologically significant length scales is not feasible. Supersaturation must be attained at the sites of frambooidal crystallization. Naturally occurring frambooidal pyrite, where present, is generally the earliest form of pyrite precipitated. Where pyrite precipitation continued, frambooids are commonly overgrown by, or recrystallized to form, coarser grained euhedral pyrite (e.g., Raiswell and Plant, 1950; England and Ostwald, 1993; Large et al., 2007; Scott et al., in prep.). Only in a few reported cases do frambooids appear to have formed again during later stages of pyrite paragenesis (e.g., Chen, 1978; this study).

The transition from frambooidal to coarser grained euhedral pyrite has been interpreted to reflect exhaustion of sources of highly reactive Fe in the immediate substrate, with a resultant decrease in the Fe content of pore fluids, requiring longer range Fe transport to the sites of pyrite precipitation (Raiswell and Plant, 1950; Raiswell et al., 1993). The absence of frambooidal pyrite formed later during pyrite paragenesis suggests that once sources of highly reactive Fe are depleted, the capacity for generating highly pyrite supersaturated pore fluids is lost in many geologic settings. However, Butler and Rickard (2000) argued that aqueous FeS cluster complexes can potentially form during the dissolution of any Fe-bearing phase. Accordingly, the range of (micro-) environments in which frambooidal pyrite may develop (via the crystallization pathway suggested by Butler and Rickard, 2000) is limited only by the requirements that FeS cluster complexes form and, together with H₂S, attain supersaturation. Indeed, Ohfuji and Rickard (2005) noted that to date, all successful laboratory syntheses of large, well-developed pyrite frambooids were for experiments conducted at higher temperatures (e.g.,
50°–350°C) than generally thought applicable to most frambooidal formation in nature (i.e., T < 20°C). They attribute this to the role of temperature in increasing reaction kinetics and suggest that frambooidal development is favored where reaction rates are high.

**Frambooidal pyrite development along dissolution surfaces**

The preferential development of frambooidal pyrite along stylolites and cleavages in Palaeozoic sedimentary rocks from northeastern Nevada and central Victoria suggests that such features locally provide suitable microenvironments for frambooidal nucleation at higher temperatures (up to at least those of lower greenschist-facies metamorphic conditions). Despite increased concentrations of pyrite and frambooidal pyrite along S2 in some samples from Fosterville, LA-ICPMS data indicates a net loss of Fe from these domains (Fig. 12). This suggests pyrite development may have been triggered, at least in part, by increased concentrations of Fe in pore waters due to the localized dissolution of Fe-bearing minerals along the cleavage. Reduced S may have been similarly derived from in situ sources (e.g., Glasson and Keays, 1978); however, marked S enrichment and δ34S zonation in the wall rocks around vein systems at most gold deposits in central Victoria (Stiwe et al., 1988; Cox et al., 1995; Gao and Kwak, 1997; Bierlein et al., 1998, 2000, 2004; Andrew et al., 2002) suggest the introduction of externally derived sulfur (e.g., H2S-bearing fluids) was also critical to pyrite formation. In this respect, it is noteworthy that Fosterville samples which have the best developed frambooidal pyrite along S2 were located immediately adjacent to bedding-parallel shear veins.

The likely importance of externally derived sulfur for sulfide development along S2 is also suggested by the work of Glasson and Keays (1978), who demonstrated that both sulfur and pyrite are generally depleted from cleavage domains in the Castlemaine Group (i.e., at greater distance from the veins). Accordingly, frambooidal nuleation adjacent to bedding-parallel veins at Fosterville is interpreted to reflect the interaction between locally sourced Fe-enriched pore waters and externally derived H2S-bearing hydrothermal fluids. In addition, many of the laminated bedding-parallel shear veins in the Castlemaine Group, including those at Fosterville, appear to have provided conduits for migrated hydrocarbons (e.g., Bierlein et al., 2001b). Petroleum, methane and/or H2S that diffused from the veins into the adjacent wall rocks may have formed bubbles or globules that provided spherical precursors for frambooidal precipitation (e.g., Rickard, 1970).

**Metal enrichment in frambooidal pyrite**

This and previous studies (e.g., Raiswell and Plant, 1980; Large et al., 2007; Scott et al., in prep.) demonstrate that frambooidal pyrite may be significantly enriched in a wide range of trace elements compared to adjacent, later formed and coarser grained pyrite. While this may principally reflect differences in the local trace metal budget at the time of pyrite formation (e.g., Raiswell and Plant, 1980; Scott et al., in prep.), the relatively rapid nucleation of frambooidal pyrite may also facilitate greater incorporation of impurities. Defect densities, caused by or capable of accommodating impurities, are likely to be highest where crystal nucleation and growth is rapid such as in frambooidal pyrite (e.g., Raiswell and Plant, 1980; Butler and Rickard, 2000). Furthermore, the relatively large surface to volume ratio of frambooidal pyrite may enhance sorption of trace elements in comparison to coarser grained pyrite (Raiswell and Plant, 1980; Bostick and Fendorf, 2003). Overprinting by soft-sediment slump and compaction features suggest that most frambooidal pyrite developed in the upper Popovich Formation on the northern Carlin trend is of early diagenetic origin. Accordingly, the consistent stratigraphic variations in trace element composition of frambooidal and other early-formed pyrite in these rocks (Scott et al., in prep.) are interpreted to reflect progressive changes in detrital input and the composition or oxidation state of basin bottom waters during sedimentation. However, similar dense clusters of frambooidal pyrite adjacent to bedding-parallel veins at Fosterville are interpreted to have formed well after sedimentation, in response to the episodic influx of hydrothermal fluids during regional deformation. In this case, elevated trace metal contents of the frambooidal pyrite may have a more exotic origin.

Many of the metals concentrated in frambooidal pyrite at Fosterville (e.g., Ag, As, Au, Mo, Pb, Sb) are interpreted to be released from sedimentary rocks during metamorphism, particularly during the transition from greenschist- to amphibolites-facies metamorphic conditions (Pitcairn et al., 2006; Large et al., 2007). Indeed, previous studies suggest that most of these elements were depleted from cleavage domains in the Orдовician shales of central Victoria (Glasson and Keays, 1978). Thus, while some trace elements incorporated into sulfides formed adjacent to bedding-parallel veins may have been partly sourced from the immediate host rocks, others (e.g., Pb enriched relative to immobile Ti in S2 cleavage domains in sample GTS_94.4. m) are more likely sourced from rocks undergoing higher grade metamorphism at greater depth. Thus, in sedimentary successions that have undergone similar deformation and metamorphic histories to those in central Victoria, sulfide distribution patterns (e.g., see Annels and Roberts, 1989), overprinting criteria, and compositional constraints on frambooidal formation should all be carefully evaluated before any genetic significance is attached to either its occurrence or metal content.

**Conclusions**

Overprinting relationships and distribution patterns for frambooidal pyrite in the sedimentary host rocks to gold deposits on the Carlin trend, Nevada, and at Fosterville, central Victoria, suggest it is not all of syngenetic or early diagenetic origin. Anomalous concentrations of frambooidal pyrite in structures formed during late diagenesis, regional deformation, and late-stage hydrothermal alteration suggest that frambooidal pyrite can form over a wide range of conditions in the upper crust and at temperatures up to at least those of lower greenschist-facies metamorphism. In such cases, frambooidal development may occur tens or hundreds of millions of years after deposition of the host rocks. The similarity of frambooids formed in syngenetic and epigenetic settings suggests a single dominant (and presumably simple) crystallization path, such as direct crystallization from dissolved reactants (e.g., Butler and Rickard, 2000; Ohfuji and Rickard, 2005), operates over a considerable depth range in the upper crust.
The development of anomalously metal-rich nodular and frambooidal pyrite in the sulfidic halos to hydrothermal veins at Fosterville, central Victoria, has implications for models of basin metallogeny. Similarly enriched frambooidal (and other texturally primitive) pyrite in deformed and metamorphosed sedimentary successions elsewhere has been interpreted as evidence for metal enrichment during sedimentation or early diagenesis (e.g., Li et al., 1998; Pitcairn et al., 2006; Large et al., 2007). However, the results of this study highlight the importance of carefully characterizing distributions and microstructural relationships before attaching genetic significance to either the occurrence or metal content of frambooidal pyrite.

Acknowledgments

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Glasson, M.J., and Keays, R.R., 1978, Gold mobilization during cleavage development in sedimentary rocks from the auriferous slate belt of central Victoria, Australia: Some important boundary conditions; ECONOMIC GEOLOGY, v. 73, p. 496–511.

Wang, G.M., and White, S.H., 1993, Gold mineralisation in shear zones within a turbidite terrane, examples from Central Victoria, S. E. Australia: Ore Geology Reviews, v. 8, p. 163–188.
Matrix Corrections to Framboidal Pyrite Pb Isotope Analyses

The relative proportions of shale matrix and pyrite in the ablated volumes was estimated from measured Al/Fe ratios for the quadrupole LA-ICPMS data as follows: Let \( A_{\text{matrix}} \) and \( F_{\text{matrix}} \) be the Al and Fe contents (ppm), respectively, of pyrite-free matrix, and \( F_{\text{py}} \sim 465,000 \) ppm be the Fe content of pyrite. If the proportion of matrix ablated in each analysis is \( X \), and the measured Al/Fe ratio is \( y \), then

\[
y = \frac{X \times A_{\text{matrix}}}{X \times F_{\text{matrix}} + (1-X) \times F_{\text{py}}}. \quad (1)
\]

Rearranging equation 1 to solve for \( X \) yields:

\[
X = \frac{y \times F_{\text{py}}}{A_{\text{matrix}} + y (F_{\text{py}} - F_{\text{matrix}})}. \quad (2)
\]

Aluminum concentrations in whole-rock geochemical data for the sequence adjacent to sample SPD213_351.90 m were used to estimate \( A_{\text{matrix}} \) and provide an internal standard with which to quantify LA-ICPMS analyses of relatively pyrite free matrix (Table 3). Once \( X \) is determined, the approximate proportions of Pb from pyrite and the matrix for each analysis were found as follows: the concentration of each of the four isotopes of Pb (\(^{206}\text{Pb}\), \(^{207}\text{Pb}\), \(^{208}\text{Pb}\)) is the sum of matrix and pyrite contributions, thus:

\[
^{n}\text{Pb}_{\text{anal}} = X \times {^{n}\text{Pb}_{\text{matrix}}} + (1-X) \times {^{n}\text{Pb}_{\text{py}}}. \quad (3)
\]

Rearranging equation 3 to solve for \(^{n}\text{Pb}_{\text{py}}\) yields:

\[
{^{n}\text{Pb}_{\text{py}}} = \frac{1}{1-X} \left[ {^{n}\text{Pb}_{\text{anal}}} - X \times {^{n}\text{Pb}_{\text{matrix}}} \right]. \quad (4)
\]

Because isotope concentrations (ppm) were determined assuming that Pb is almost entirely contained in pyrite (i.e., \( F_{\text{py}} \) used as internal standard) measured concentrations \(^{n}\text{Pb}_{\text{anal}}\) do not represent the actual Pb concentration for the ablated volume, as required in equation 4. However, where Pb contributions from other sources (e.g., matrix) represent a small fraction of the total measured Pb (i.e., \(^{n}\text{Pb}_{\text{anal}} = {^{n}\text{Pb}_{\text{py}}} \)), the multiplication factor on the right side of equation 4 can be neglected, and a revised estimate of \(^{n}\text{Pb}_{\text{py}}\), which approximately accounts for the matrix Pb component, is given by:

\[
{^{n}\text{Pb}_{\text{py}}} = {^{n}\text{Pb}_{\text{anal}}} - X \times {^{n}\text{Pb}_{\text{matrix}}}. \quad (5)
\]

The total concentrations of each Pb isotope (i.e., \(^{n}\text{Pb}_{\text{anal}}\) in eq. 5) in each analysis were determined using measured values of \(^{204}\text{Pb}/^{204}\text{Pb} \), \(^{207}\text{Pb}/^{204}\text{Pb} \), \(^{206}\text{Pb}/^{204}\text{Pb} \) isotopic ratios and total measured Pb concentration. Two different matrix compositions were used to model the likely matrix Pb contributions to frambooidal pyrite analyses in sample RHD019_161.42 m (Table 4A-B). In Model 1 the Pb isotope composition of the matrix is based on data for sample SPD213_351.90 m (Fig. 17A, Table 3), and in Model 2 a more radiogenic composition based on LA-ICPMS data for a relatively pyrite free area in sample RHD019_161.42 m is used (Fig. 17B, Table 3).
3). Results for both models indicate that for matrix Pb contents in the range 25 to 90 ppm Pb, the matrix only contributes significantly to measured Pb isotope ratios for ablation volumes containing <10 percent frambooidal pyrite.

Corrections to the measured $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios based on the estimated matrix proportion are similar to corrections accounting for the U contents of the ablated volumes (quadrupole ICPMS data only, Fig. 17C) based on the following formulas:

$$
\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_{\text{corr}} = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_{\text{meas}} \left[1 - \left(\frac{^{238}\text{U}/^{206}\text{Pb}}{^{235}\text{U}/^{206}\text{Pb}}\right)_{\text{meas}} \times e^{k_2 t} - 1\right], \tag{6a}
$$

$$
\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_{\text{corr}} = \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_{\text{meas}} \left[1 - \left(\frac{^{238}\text{U}/^{206}\text{Pb}}{^{235}\text{U}/^{206}\text{Pb}}\right)_{\text{meas}} / 137.9 \times e^{k_1 t} - 1\right], \tag{6b}
$$

where $k_1$ ($= 1.55125 \times 10^{-10}$ y$^{-1}$) and $k_2$ ($= 9.8485 \times 10^{-10}$ y$^{-1}$) are the decay constants for $^{238}$U and $^{235}$U, respectively, $t$ is the maximum crystallization age (y) and 137.9 is the ratio of $^{238}$U/$^{235}$U.