

This is the peer reviewed version of the following article: Fougrouse, D. and Micklethwaite, S. and Halfpenny, A. and Reddy, S. and Cliff, J. and Martin, L. and Kilburn, M. et al. 2016. The golden ark: Arsenopyrite crystal plasticity and the retention of gold through high strain and metamorphism. *Terra Nova*. 28 (3): pp. 181-187, which has been published in final form at <http://doi.org/10.1111/ter.12206> This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving at <http://olabout.wiley.com/WileyCDA/Section/id-828039.html>

1 The golden ark: Arsenopyrite crystal plasticity and the  
2 retention of gold through high strain and metamorphism.

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18

19 **ABSTRACT**

20 Quantitative electron backscatter diffraction analysis and ion microprobe imaging of gold-rich  
21 arsenopyrites provide the first insights into the crystal plasticity and element mobility  
22 behaviour of arsenopyrites through metamorphism (340° - 460° and 2 kbars). Remarkably, the  
23 gold-rich arsenopyrites remained structurally and chemically robust during high strain  
24 deformation. It is only during a superimposed lower strain deformation event, at a high angle

25 to the preferred orientation of the arsenopyrites, that small amounts of crystal plasticity affected  
26 the arsenopyrites. During the low strain event a dissolution-reprecipitation reaction resulted in  
27 loss of gold from the crystal lattice, facilitated by localised domains of recrystallization, most  
28 likely due to fluid percolation along sub- and new grain boundaries. We suggest the abundance  
29 and rheologically robust nature of gold-rich arsenopyrite in giant gold deposits, affected by  
30 greenschist-amphibolite metamorphism, is actually a critical factor in the preservation of those  
31 deposits.

32

### 33 **INTRODUCTION**

34 Although rarely acknowledged, arsenopyrite is one of the world's most important  
35 sulphide minerals. It is ubiquitous as a gold bearing phase in many giant deposits, particularly  
36 in sediment hosted orogenic gold deposits (Groves et al., 1998) as documented at Obuasi,  
37 Ghana, (Oberthür et al., 1994), Sunrise Dam, Australia (Sung et al., 2009), Muruntau,  
38 Uzbekistan (Morelli et al., 2007) or Red Lake, Canada (Dubé et al., 2004). The presence of  
39 arsenic and arsenopyrite also provide important vectors to mineral resources (Boyle and  
40 Jonasson, 1973; Eilu and Groves, 2001; Le Vaillant et al., 2015). For these reasons it is  
41 surprising that almost nothing is known about the crystal plasticity of arsenopyrite, nor the  
42 influence of microstructure on the ability of arsenopyrite to retain or release its major and trace  
43 element content.

44 In contrast to arsenopyrite, the crystal plasticity of other sulphide phases such as pyrite,  
45 pyrrhotite, sphalerite, chalcopyrite, galena, stibnite and pentlandite have been investigated in  
46 detail (Barrie et al., 2011; Boyle et al., 1998; Cox, 1987; Kelly and Clark, 1975; Vukmanovic  
47 et al., 2014). These studies conclude that crystal plasticity of phases, such as pyrite, occurs  
48 relatively easily at temperatures as low as 260 °C and strain rates of approximately  $10^{-12}$  -  $10^{-$

49  $16 \text{ s}^{-1}$  (Barrie et al., 2011) and can have a significant impact on trace element mobility (Reddy  
50 and Hough, 2013).

51 Here we provide the first documentation of arsenopyrite crystal plastic behaviour under  
52 high strain and greenschist facies metamorphic conditions. We examine the impact on trace  
53 element modification, with important implications for both resource preservation and the  
54 release of elements from arsenopyrite back to the natural environment.

55

## 56 **SAMPLES AND METHODS**

57 In order to examine the crystal-plastic behaviour of arsenopyrite and its impact on trace  
58 element mobility, arsenopyrites with large enrichments of trace elements (Au, Ni) and well-  
59 constrained metamorphic-strain conditions were selected from the economic refractory ores of  
60 the giant Obuasi deposit. The mineralized arsenopyrites are hosted in paleoproterozoic sheared  
61 phyllites (2155 Ma, zircon U/Pb maximum age of deposition; Oberthür et al., 1998) composed  
62 of micas, quartz, carbonates (ankerite and siderite), chlorites, rutile and graphite. Arsenopyrite  
63 growth and mineralization occurred during continuous cleavage development and peak upper  
64 greenschist metamorphism at  $340^{\circ}$  -  $460^{\circ}$  and 2 kbars as shown by the development of strain  
65 shadows parallel with the continuous cleavage surrounding the arsenopyrites (the Eburnean  
66 orogeny: Schwartz et al. 1992; Oberthür et al. 1994; Fougrouse et al. in press). A large sample  
67 suite (>200 samples) was collected and studied from mineralised exposures of the Obuasi mine  
68 to provide representative petrographical and geochemical results across the deposit. Two grains  
69 from sample 215-20 are reported in this study, collected ~950 m below the surface from a 10  
70 m wide high strain domain associated with thick quartz veins, between two graphitic shear  
71 zones. The arsenopyrites have been subject to two strain events (Fougrouse et al., in press-b),  
72 mostly accommodating pure shear. The first event is high strain, at the peak of metamorphism,  
73 which occurred during the Eburnean orogeny (D2<sub>Ob</sub>; Fougrouse et al., in press). A pervasive

74 continuous cleavage developed while the quartz veins underwent boudinage and strain shadows  
75 developed around the arsenopyrite grains (Fig. 1). The long-axes of the acicular arsenopyrites  
76 (up to 0.1x1 mm) are aligned parallel to the cleavage. A large minimum finite strain of 48%  
77 shortening and 235% stretch, perpendicular to the shortening, was estimated for the hosting  
78 phyllites from strain shadow length and fold periodicity (Fig. 1; p. 271 Ramsay and Huber,  
79 1983), using oriented thin sections cut orthogonal to the cleavage and parallel to the lineation.  
80 Nonetheless, the arsenopyrite grains themselves remain largely euhedral and relatively  
81 undeformed (Fig. 2). In the second event (D3<sub>Ob</sub>), a low strain overprinting crenulation cleavage  
82 developed, representing a minimum shortening estimated at 15% with no associated stretch.  
83 The long-axes of the arsenopyrites are oriented at a high angle to the later crenulation cleavage.

84 Backscattered Scanning Electron Microscopy imaging (BSE) and Secondary Ion Mass  
85 Spectrometer (SIMS and NanoSIMS) investigations were carried out at the Centre for  
86 Microscopy, Characterisation and Analysis, University of Western Australia. BSE images were  
87 collected using a TESCAN VEGA3 SEM and large area ion imaging of <sup>197</sup>Au were performed  
88 on a Cameca IMS 1280 ion probe on 150x150 micron areas using a ~1 micron, Cs<sup>+</sup> primary  
89 beam. Ions were collected in peak-hopping mode in an ion-counting electron multiplier at a  
90 mass resolution of ~3000. High-resolution elemental mapping was carried out using the  
91 Cameca NanoSIMS 50 with a spot size of approximately 100 nm and a Cs<sup>+</sup> primary beam. The  
92 experiment allowed simultaneous detection of <sup>197</sup>Au and <sup>34</sup>S across areas measuring 100 x 100  
93 μm with a 120 nm/pixel resolution. Quantitative orientation maps of arsenopyrite crystal lattice  
94 were recorded using EBSD (Prior et al., 1999) at the CSIRO Earth Science and Resource  
95 Engineering in Kensington (Australia) using a Zeiss Ultraplus FEG SEM and at Curtin  
96 University using a TESCAN MIRA3 SEM. Systematic mis-indexing due to pseudosymmetry  
97 within the arsenopyrite grains was removed by identifying the axis and angle relationships to  
98 rotate the points and produce a correctly indexed grain. It should be noted that pseudosymmetry

99 is a problem in pyrite and arsenopyrite. Correcting for pseudosymmetry can produce internally  
100 consistent datasets, although the actual solution may still be wrong (Nolze et al., 2016),  
101 however in this study such issues do not change our conclusions.

102

## 103 **RESULTS**

104 Arsenopyrites from the ore zone of the Obuasi deposit are composed of two primary  
105 domains: rims that appear homogenous in BSE images (A-rims) and inclusion-rich internal  
106 cores. The cores contain inclusions of pyrrhotite, chalcopyrite or rutile. There is then a  
107 discontinuously developed third domain (B-rims) crosscutting all others (Fig. 3). B-rims are  
108 characterised by higher arsenic concentrations (~46 wt% as opposed to ~44 wt% in A-rims;  
109 Fougere et al. in press) and preserve the original shape of the crystals. The B-rim contacts  
110 are sharp, planar to curvilinear (bulbous) and penetrate in from microcracks and grain  
111 boundaries (Fig. 3).

112 The EBSD data show a relative change in crystallographic orientation for each grain (Fig.  
113 2 and 3). Consistent with other studies investigating sulphides crystal-plasticity (Reddy and  
114 Hough 2013), we define high-angle grain boundaries to have misorientations  $\geq 10^\circ$ . All  
115 boundaries  $< 10^\circ$  are low-angle grain boundaries, representing subgrains. In most cases the  
116 intragrain variation does not reach  $5^\circ$ , though new grains are formed at a few localised points.

117 The analysis reveals a difference in the deformation intensity between grain 1 and 2 (Figs.  
118 2 and 3). Grain 1 is parallel to the main cleavage ( $S_{2Ob}$ ), in a domain unaffected by the later  
119 crenulation cleavage ( $S_{3Ob}$ ), and contains only weak internal deformation (maximum of  $3^\circ$   
120 misorientation). Conversely, grain 2 is located on a fold flexure of the  $S_{3Ob}$  crenulation. In this  
121 crystal, high densities of misorientations occur in a narrow localised domain, adjacent to a  
122 fracture filled with pyrite (Fig. 3D). In this domain, the misorientations define low- and high-  
123 angle boundaries creating new small sized grains. In the centre top of the grain an incipient

124 domain of less than  $3^\circ$  misorientation is developed. The cumulative orientation profiles (Fig.  
125 3H) along the short axis of grain 2 show minor misorientations ( $<2^\circ$ ), but much greater  
126 misorientations are achieved parallel to the long axis of the arsenopyrite (up to  $7^\circ$  from the tip  
127 of the grain to the core). Pole figure data indicates a dispersion of the orientation (Fig. 3). In  
128 addition, the pyrite crystal infilling the fracture of grain 2 is virtually undeformed  
129 (misorientation up to  $2^\circ$ ; Fig. 3C).

130 The SIMS and NanoSIMS  $^{197}\text{Au}$  ion microprobe imaging reveals that the distribution of  
131 the gold is zoned within the crystals, with gold-rich A-rims around gold-poor cores (Fig. 2 and  
132 3). The A-rims are in turn crosscut by gold-poor B-rims (Fig. 3F). The A-rims represent  
133 epitaxial zones with up to 1000 ppm Au (Fisher et al., 2014; Oberthür et al., 1994), although  
134 these concentrations decrease on the outer edges of the grain as shown on the left side of grain  
135 2 (Fig. 3). An A-rim is well developed in grain 1 where minimal internal deformation occurred.  
136 In grain 2, a large A-rim is cut by discontinuous B-rims, characterized by low Au signal.  
137 Internally, the A-rims are finely zoned with submicron-scale concentric bands with sharp  
138 boundaries (Fig. 3F; Fougrouse et al. in press GCA). However, this fine epitaxial zoning in  
139 the domain of high misorientation identified in grain 2, appears blurry, with diffuse boundaries  
140 between bands and locally, small spherical high Au concentrations. The fuzzy gold signal in  
141 this domain is also dissected by numerous small scale, sharply defined B-rims with low Au  
142 signals. Critically, the overall B-rim width in this region of high densities of misorientations is  
143 up to three times greater in comparison with the domains of undeformed arsenopyrite.

144

## 145 **CRYSTAL-PLASTIC EVOLUTION OF ARSENOPYRITES AND CONSEQUENCES** 146 **FOR GOLD RETENTION**

147 The crystallographic misorientations and localised intragrain textures, revealed by EBSD,  
148 are consistent with dynamic recrystallisation by dislocation creep (Hirth and Tullis, 1992; Urai

149 et al., 1986). In grain 2, this led to the development of subgrains and neoblasts accommodating  
150 crystal-plastic strain in a narrow localised domain, on the top right-hand side of the crystal.  
151 This crystal-plastic strain domain is coincident with a fracture filled with undeformed pyrite  
152 (Fig. 1). Overall, several significant features emerge from our analysis.

153 Firstly, grain 1 and grain 2 formed during high strain ( $D2_{Ob}$ , 50% flattening, >200%  
154 stretch) and upper greenschist metamorphism (John et al., 1999; Schwartz et al., 1992), then  
155 were subject to a second shortening event ( $D3_{Ob}$ , ~15% shortening), yet remained euhedral and  
156 underwent only minor crystal-plastic deformation. Secondly, grain 1 has minimal lattice  
157 distortion ( $\leq 3^\circ$  of misorientation from grain tip to centre) in comparison to grain 2, which  
158 contains a localized domain of subgrains, neoblasts and microfracture. In this regard, grain 1  
159 is located parallel to the  $S2_{Ob}$  cleavage, in a microlithon between two crenulation planes ( $S3_{Ob}$ ),  
160 while grain 2 is located on a fold flexure of the  $S3_{Ob}$  cleavage. These relationships indicate that  
161 crystal plastic microstructures developed not during the high strain peak metamorphic event  
162 but during microfolding in the lower strain  $D3_{Ob}$  event, which only affected grain 2. Consistent  
163 with this interpretation, the orientation profiles (Fig. 3H) show that crystal-plasticity and the  
164 largest amount of lattice misorientation is recorded parallel to the  $D3$  shortening direction. As  
165 the fold grew, the arsenopyrite firstly underwent crystal-plastic deformation, then a fracture  
166 propagated through the arsenopyrite in the hinge, perhaps facilitated by embrittlement related  
167 to crystal-plastic strain hardening (Fleck et al., 1994). The fracture is infilled with undeformed  
168 pyrite (misorientation  $< 2^\circ$ ), again indicating the arsenopyrite crystal-plasticity occurred early  
169 during  $D3_{Ob}$  microfolding.

170 We conclude arsenopyrite is remarkably resilient to crystal plasticity at the recorded  
171 temperatures of  $340^\circ - 460^\circ$  and pressures of 2 kbars. Two factors likely contribute to this  
172 resilience. Arsenopyrite is monoclinic (Bindi et al., 2012), which means only a limited number  
173 of slip systems are available for activation. In addition, arsenopyrites are acicular with a strong



174 shape preferred orientation (SPO). Because there is a competency contrast between  
175 arsenopyrite and the quartz-phyllsilicate rich wall rock, at upper greenschist conditions, the  
176 SPO allows for accumulation of large strains in the wall rock, while grains aligned with the  
177 cleavage remain undeformed (Jessell et al., 2009). We acknowledge that crystal plasticity could  
178 be more advanced where arsenopyrites impinge on one another (Barrie et al., 2010), but in this  
179 case the percentage of such arsenopyrites was >1% at Obuasi.

180 Furthermore, our results show B-rims with sharp boundaries cutting primary gold  
181 zonation, enriched in As and depleted in Au, but preserving the morphology and  
182 crystallographic orientation of the parent arsenopyrite. These relationships are indicators that  
183 a pseudomorphic dissolution-reprecipitation reaction (Harlov et al., 2011; Putnis, 2009) has  
184 resulted in loss of trace element content (gold) from the crystal lattice. The compositional  
185 difference between A- and B-rims indicates that re-equilibration to a more stoichiometric  
186 composition was the driving force behind the replacement reaction (Geisler et al., 2007).

187 The texture of the gold zoning in the recrystallized domains of grain 2 (Fig. 3), is blurry  
188 and diffuse, in apparent contradiction to the sharp oscillatory zoning of the undeformed  
189 domains. This texture can be explained by volume diffusion and migration of dislocations  
190 during crystal lattice deformation, i.e. dislocation–impurity pair (DIP) diffusion model  
191 (Vukmanovic et al., 2014). Critically, in this same domain, the B-rim gold-poor replacement  
192 zones penetrate further (up to three times greater), highlighting a link between crystal-plastic  
193 microstructure and facilitation of reaction. We suggest that domains of crystal-plastic  
194 microstructure (Fig. 3) increased the porosity along high and low angle crystallographic  
195 boundaries (Timms et al., 2012), facilitating the reaction by enhanced mobility of components  
196 to and from the reaction front (Fig. 4).

197

198 **CONCLUSIONS**

199           The implications of our observations for trace element retention and loss in arsenopyrites  
200 are profound.

201     • Arsenopyrite is robust, maintaining its trace element content through conditions of high  
202       wall rock strain and metamorphism. This behaviour stands in contrast to other sulphides  
203       such as pyrite, characterized by multiple slip systems that can be activated at temperatures  
204       as low as 260 °C (Barrie et al., 2011; Reddy and Hough, 2013).

205     • Such robust properties for arsenopyrite contribute to our understanding of its common  
206       association with world-class gold deposits. The ability of arsenopyrite to absorb gold into  
207       the crystal lattice and as nanoparticles (Cabri et al., 2000) establishes a clear link with  
208       mineralisation. Perhaps more importantly, its ability to maintain such trace element content  
209       through high strains means that precious metal resources are then preserved in the rock  
210       record. In this manner, arsenopyrite acts like an ark, encapsulating and preserving precious  
211       metals or trace elements.

212     • Figure 4 presents our model of the microstructural response of arsenopyrite to strain, and  
213       associated loss of trace elements (gold). Internal deformation only occurs during  
214       crenulation of rock fabrics, when arsenopyrites become aligned with the principal  
215       contraction direction. Microfolding is accommodated by localised zones of crystal-plastic  
216       deformation, strain-hardening and subsequent microfracture. Where crystal-plastic  
217       microstructures are developed, they enhance the release of gold from arsenopyrites  
218       undergoing reaction back to the natural environment.

219     • Although the analyses presented here from two arsenopyrites are representative of a large  
220       population of arsenopyrites from Obuasi, which we examined petrographically, we  
221       recommend future studies of arsenopyrite and other sulphides incorporate EBSD analysis  
222       to confirm these results and better understand the role of microstructure in modifying gold  
223       deposits.

224

225 **ACKNOWLEDGMENTS**

226 This study derives from Ph.D. research by DF. AngloGold Ashanti is acknowledged  
227 for excellent financial support and field assistance. The Centre for Microscopy,  
228 Characterisation & Analysis, University of Western Australia, is funded by the University,  
229 State and Commonwealth Governments. SM was funded by the Hammond-Nisbet Endowment.

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337

338 FIGURE CAPTIONS

339 Figure 1. A) Boudinaged mineralized quartz vein, Obuasi underground mine; B) Micrograph  
340 of mineralized metasedimentary ore, comprising gold-bearing arsenopyrites with quartz strain  
341 shadows deformed by a crenulation cleavage; C) Schematic of shear strain calculation  
342 estimation and equations used in D (modified after Ramsay and Hubert 1983); D) Frequency  
343 of shear strain ( $e_{\text{stretch}}$ ) calculated from 100 strain shadows surrounding arsenopyrites.

344

345 Figure 2. Sample 215-20, grain 1 - the arsenopyrite boundaries, cores and rims are highlighted  
346 in red. A) Backscattered electron (BSE) image; B) Cumulative orientation profile along line a-  
347 a' (plotted relative to point a) parallel with the arsenopyrite long axis. Only minor  
348 crystallographic misorientations are recorded in the grain despite the wall rock being subject  
349 to high strain. C) Coloured EBSD maps showing crystallographic misorientations in the range  
350 0-10°. Position of orientation profile a-a' is indicated; D) SIMS elemental gold distribution  
351 map. The arsenopyrite is zoned with gold-poor core and gold-rich rim (A-rim).

352

353 Figure 3. Sample 215-20, grain 2 - the arsenopyrite boundaries, cores and rims are highlighted  
354 in red; A-B) Backscattered electron (BSE) images; C-D) Coloured EBSD maps, showing  
355 crystallographic misorientations in the range 0-10° for C and 0-90° for D. Grain 2 coincides  
356 with a crenulation microfold and is weakly deformed by this later overprinting low strain event  
357 ( $D3_{\text{Ob}}$ ), especially in zone D. High-angle boundaries ( $\geq 10^\circ$ ) are plotted in black and low-angle  
358 boundaries ( $\geq 2^\circ$ ) in red. Dynamic recrystallization has produced subgrains and new grains.  
359 Position of orientation profiles a-a' and b-b' are indicated; E) SIMS elemental map of  $^{197}\text{Au}$ ;  
360 F) NanoSIMS composite image of  $^{197}\text{Au}$  (yellow) and  $^{34}\text{S}$  (blue) elemental distribution. B-rims  
361 are gold depleted in comparison to A-rims, and are well developed around zone F; G) Pole

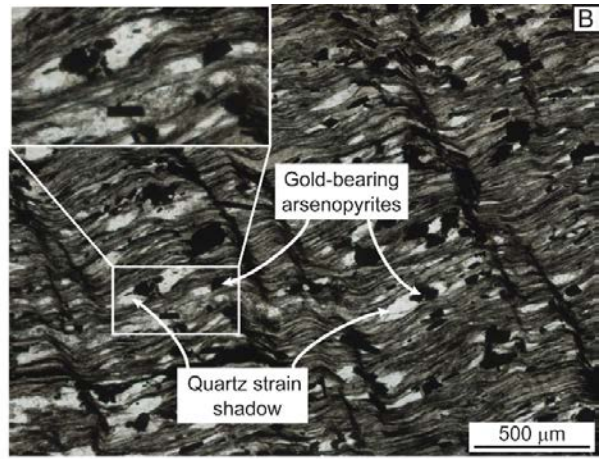
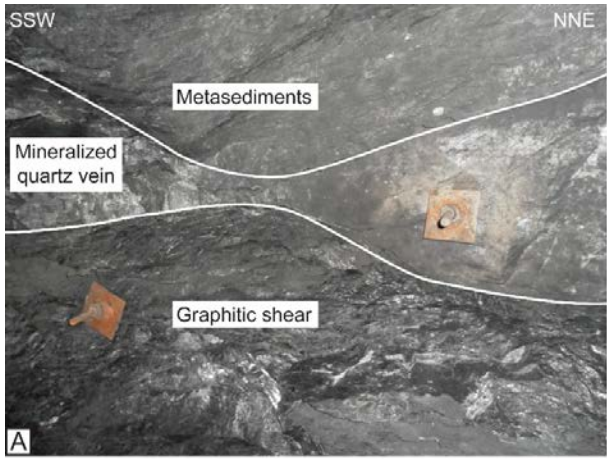


362 figures show the dispersion of orientation data; H) Cumulative orientation profiles (plotted  
363 relative to first point) parallel with the long axis (a-a') and short axis (b-b') of grain 2. The  
364 largest crystallographic misorientations are recorded along the crystal long axis (a-a'), parallel  
365 with the D3 shortening direction.

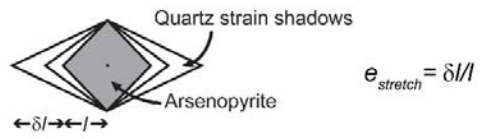
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367 Figure 4. Interpretation of the microstructural deformation sequence and replacement of  
368 arsenopyrite grain 2.

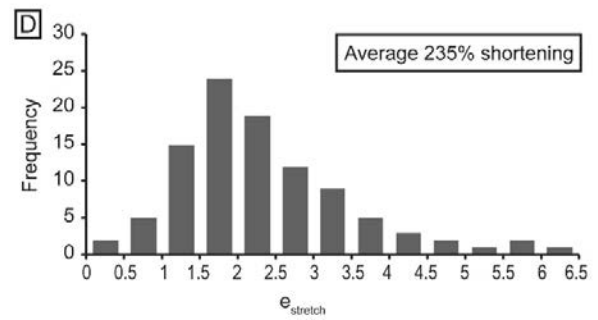
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C Stretching estimation: Strain shadow geometry

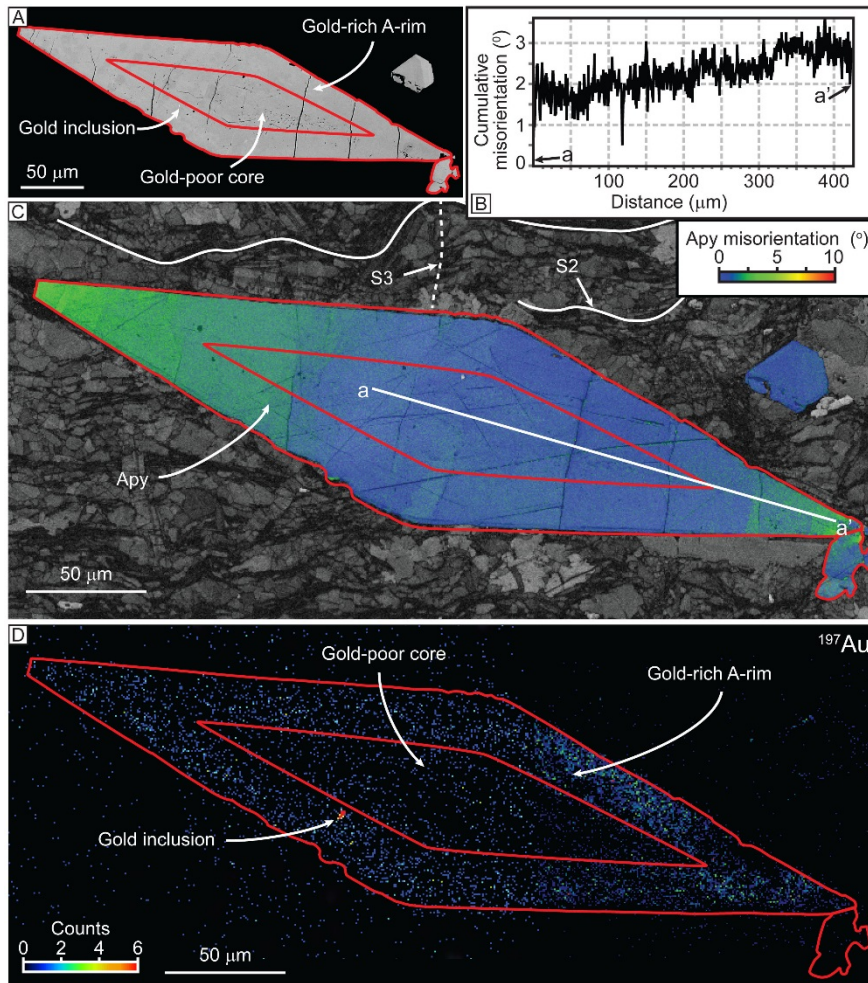


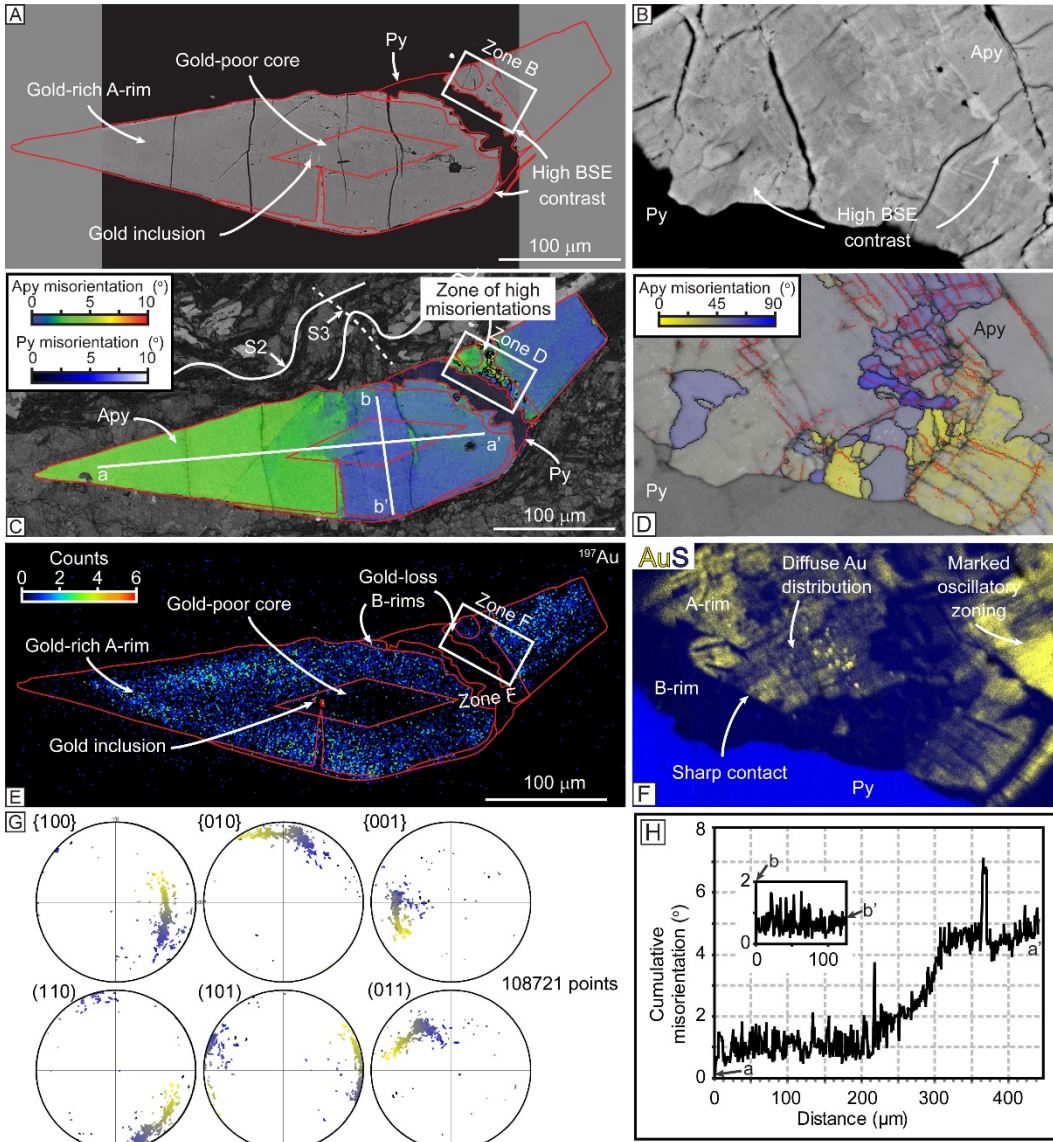
Shortening estimation: Fold geometry



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