Geometry and genesis of the giant Obuasi gold deposit, Ghana

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This thesis is presented for the degree of Doctor of Philosophy.

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"It never gets easier, you just go faster"

Gregory James LeMond
The supergiant Obuasi gold deposit is the largest deposit hosted in the Paleoproterozoic Birimian terranes of West Africa (62 Moz, cumulative past production and resources). The deposit is hosted in Kumasi Group sedimentary rocks composed of carbonaceous phyllites, slates, psammites, and volcanioclastic rocks intruded by different generations of felsic dykes and granites.

In this study, the deformation history of the Obuasi district was re-evaluated and a three stage sequence defined based on observations from the regional to microscopic scale. The $D_{1_{\text{Ob}}}$ stage is weakly recorded in the sedimentary rocks as a layer-parallel fabric. The $D_{2_{\text{Ob}}}$ event is the main deformation stage and corresponds to a NW-SE shortening, involving tight to isoclinal folding, a pervasive subvertical $S_{2_{\text{Ob}}}$ cleavage striking NE, as well as intense sub-horizontal stretching. Finally, a N-S shortening event ($D_{3_{\text{Ob}}}$) formed an ENE-striking, variably dipping $S_{3_{\text{Ob}}}$ crenulation cleavage.

Three ore bodies characteristic of the three main parallel mineralised trends were studied in details: the Anyankyerem in the Binsere trend; the Sibi deposit in the Gyabunsu trend, and the Obuasi deposit in the main trend. In the Obuasi deposit, two distinct styles of gold mineralisation occur; (1) gold-bearing sulphides, dominantly arsenopyrite, disseminated in metasedimentary rocks and (2) native gold hosted in quartz veins up to 25 m wide. Both mineralisation styles are contained in high grade ore shoots classified in three groups on the basis of 3D modelling of deposit geometry from drill hole and underground development data; (1) volcanic rock controlled shoots, (2) fault intersection and bifurcation, and (3) $F_{3_{\text{Ob}}}$ fold hinge controlled shoots. Strain shadows surrounding gold-bearing arsenopyrite parallel with $S_{2_{\text{Ob}}}$ but folded by $S_{3_{\text{Ob}}}$, indicate that the sulphides were formed during $D_{2_{\text{Ob}}}$. In contrast, although the mineralised quartz veins formed during $D_{2_{\text{Ob}}}$, field, SEM and microtomographic observations demonstrate that the gold is hosted in microcrack networks in the veins, located in hinges of $F_{3_{\text{Ob}}}$ folds. These observations provide the first evidence for multiple stages of gold deposition at the Obuasi deposit.

The crystal plasticity and element mobility behaviour of the gold-bearing arsenopyrite during metamorphism ($340^\circ - 460^\circ$ and 2 kbars) was investigated using quantitative electron backscatter diffraction analysis, ion microprobe imaging and synchrotron XFM mapping. The results show that the arsenopyrites remained remarkably robust during the high strain deformation ($D_{2_{\text{Ob}}}$) and preserved their gold content (300 to 3000 ppm Au). However, small amounts of crystal plasticity or intragranular microcracking, during $D_{3_{\text{Ob}}}$, enabled low volume fluid infiltration into the arsenopyrites and activation of a dissolution-replacement reaction, involving replacement by Au-poor (below detection limit of all techniques), Ni-
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rich (up to 3000 ppm Ni) arsenopyrite coeval with Ni-rich pyrite and native gold precipitation in the microcracks. The newly formed arsenopyrite is also S- and Fe-depleted and As-enriched in comparison to the primary arsenopyrite. Thin-section scale mass balance calculations indicate gold was mobilised over distances greater than the centimetre scale; likely contributing to native gold along wall rock cleavage and at high concentrations in the fracture networks of the quartz veins. The gold remobilisation mechanism was likely controlled by strong chemical gradients at crystal-fluid interfaces induced by the salinity of the infiltrating fluid and S-release during the replacement reaction. It is suggested that the high grade native gold hosted in quartz veins was sourced from the arsenopyrite mineralisation.
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Acknowledgements

Here we are, 3.5 years from the start. The thesis is printed, finished, submitted. More than an ending point, I see this moment as a beginning, ready to further investigate the world of geology. I gained more than a degree here, but a wide range of skills and expertise as well as personal enrichment. This is what I am most grateful of and this has been accomplished with the help of many people.

On top of the list, my supervisors, Steve Micklethwaite, Stano Ulrich, John Miller and Cam McCuaig. So much has been done with their help, particularly Steve who gave some top quality guidance and was always available for scientific and personal discussions through corridor meetings, Skype calls and countless emails. Thank you for that. The departure of Stano after the first year was heartbreaking, but Stano was always present and willing to help out. Thank you. John and Cam made this project possible and they too, were excellent advisors. Thank you both.

Secondly, AngloGold Ashanti Ltd is gratefully acknowledged for its financial and logistic support. Jane Allen and Tom Gell managed this project with care and have been very comprehensive in releasing scientific communications. The Obuasi operations team logistic help, in particular Clement Asamoah-Owusu and Wisdom Kportufe, during the numerous field missions, was priceless. Thank you for everything.

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I also give the thumbs up to the Centre for Exploration Targeting and School of Earth and Environment students, past and present, there is only one word to describe you all: Legends.

Last but by no means least, my wonderful partner in life, Lisa, and my family. Thank you for your constant support and also for not understanding geology. This has helped me on an everyday basis to separate work stress and home time. I can’t be grateful enough for having you.
Chapter I: Introduction

Geometry and genesis of the giant Obuasi gold deposit, Ghana

1. Context and aim of this thesis

1.1. Context

The trade of gold in the Ashanti region of Ghana can be traced as far back as the 10th century AD. During the 15th century gold trade between West Africa and Europe brought wealth and power to the Ashanti Kingdom and the region was renamed after the noble metal, the Gold Coast (Wilks, 1993). Obuasi, or “under the rock” translated from the local Twi language, certainly played an important role in this wealth with the local gold seekers, the Galamsey, panning and digging extremely gold-rich quartz veins cropping out at the surface (Ayensu, 1997). The Obuasi gold deposit, also named the Ashanti mine, is today the largest known economic concentration of gold mineralisation in the Paleoproterozoic West African craton. Industrial mining officially started in 1897 in the form of the newly established Ashanti Goldfields Corporation. In 2014, the cumulative past production and resource reached 62 Moz of gold (AngloGold-Ashanti, 2014).

Numerous geological studies have carefully documented general or more specific aspects of the Obuasi deposit’s geology (Junner, 1932; Wilson, 1972; Amanor, 1979; Gyapong, 1980; Bowell et al., 1990; Oberthür et al., 1991; Schwartz et al., 1992; Blenkinsop et al., 1994; Höhndorf et al., 1994; Mücke and Dzigbodi-Adjimah, 1994; Oberthür et al., 1994; Klemd et al., 1996; Oberthür et al., 1996; Mazzucchelli, 1997; Mumm et al., 1997; Oberthür et al., 1998; Yao and Robb, 2000; Yao et al., 2001; Allibone et al., 2002b; Fougerouse et al., 2013; Fougerouse et al., in press). Arguably, the most controversial topics revolve around the structural evolution of the Obuasi deposit during the Eburnean orogeny (Blenkinsop et
al., 1994; Allibone et al., 2002b; Fougerouse et al., in press), the relative timing of mineralisation and ore shoots controls (Blenkinsop et al., 1994; Oberthür et al., 1994; Allibone et al., 2002b; Fougerouse et al., 2013; Fougerouse et al., in press), and the fluid inclusion chemistry (Schwartz et al., 1992; Klemd et al., 1996; Mumm et al., 1997; Klemd, 1998; Mumm et al., 1998; Yao and Robb, 2000; Yao et al., 2001).

1.2. **Aim and objectives of this thesis**

This thesis aims to provide a new understanding of the geology and genesis of the Obuasi deposit, integrating the previous studies alongside new data and interpretations. The approach undertaken was multi-scale and multi-disciplinary, using a wide range of tools from 3D modelling of the large drill core dataset alongside open pit and underground mapping, to microanalyses from techniques such as XFM synchrotron elemental imaging, electron backscatter diffraction and high-resolution secondary ion microprobe. The central aim was to understand the geological evolution and metallogenic processes involved in the formation of the largest gold deposit in West Africa. The novel combination of techniques utilised in this study provided outstanding opportunities to examine the grain-scale mechanisms involving deformation, reaction and gold mobility.

In addition to these scientific objectives, there were obligations to the industry sponsor of this study, AngloGold Ashanti Ltd. AngloGold Ashanti Ltd required a better understanding of the deposit in order to improve their exploration strategy. Amongst others, the main questions were as follows: (1) How has the 3D structural architecture of the deposit evolved through time? (2) Are there early syn-sedimentary faults structures controlling the later syn-gold fault architecture and emplacement of intrusions? (3) What are the controls on the geometry of the ore body and the high grades ore shoots? (4) How many mineral alteration events occurred and how do they interact in space and time? (5) Was there more than one fluid in the mineral system? (6) Can an alteration footprint be defined for each fluid type identified that can be used in targeting?

Results and progress of the research work were communicated throughout the project by quarterly reports and presentations. Although some of the results from this partnership remain confidential, AngloGold Ashanti Ltd agreed to release most of this work to a wider audience with 5 manuscripts cleared for publication, 2 extended abstracts and multiple (5) presentations at conferences. The final report of the project cannot be included in this thesis, however the main outcomes are summarised in chapter VI.
2. Methodology

This section provides here a summary of each method used in the course of the research. More details are provided in subsequent chapters.

2.1. Field observations, mapping and sample collection

As outlined in more detail in Chapter II, open pit exposures from each mineralised trend and underground exposures from the Obuasi mine were studied and mapped. All active areas of the mine were studied. Both fabric form line and lithological boundary mapping techniques were followed. On the basis of the field observations, 224 samples were collected from outcrop, underground exposure, and drill core, in order to provide a representative database of fault rocks, fabrics, alteration, and ore zones. Geotechnical drill holes have been used to collect representative least altered samples further away from the mineralisation.

2.2. Analytical techniques

2.2.1. Optical microscopy

Strain fabric characterisation, mineral identification, overprinting relationships, and paragenesis were investigated with transmitted and reflected light optical microscopy. This enabled characterisation of the petrology and overprinting relationships and prioritisation of samples for higher resolution analyses and electron microscopy.

2.2.2. Scanning Electron Microscopy

Scanning electron microscopy (SEM) and backscattered electron images (BSEM) were generated using a TESCAN VEGA3 SEM at the Centre for Microscopy, Characterisation & Analysis (University of Western Australia). Energy Dispersive X-ray spectra (EDX) were acquired using an Oxford instruments X-Max 50 silicon drift detector with AZtec software fitted on the TESCAN VEGA3.

2.2.3. Electron Probe Microanalyzer

A JEOL JXA-8530F field-emission gun hyperprobe (EPMA) was used for microchemical characterisation of gold-bearing arsenopyrite grains at the Centre for Microscopy, Characterisation & Analysis (University of Western Australia).
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2.2.4. **High resolution X-ray computed tomography**

To investigate the 3D distribution and geometric relationships of the native gold in the quartz veins, a 25 mm core of a high-grade quartz sample was scanned using the XRADIA Versa XRM 500 3D X-ray microscope, installed at the Australian Resource Research Centre (CSIRO, Kensington, Australia).

2.2.5. **Electron Backscattered Diffraction**

Electron backscatter diffraction (EBSD) and EDS data were collected at Australian Resource Research Centre (CSIRO, Kensington) using a Bruker e-flash detector for EBSD and a Bruker XFlash 5030 silicon drift detector for EDS, fitted on a Zeiss Ultraplus FEG SEM.

2.2.6. **Ion probe imaging (SIMS and NanoSIMS)**

Ion imaging in arsenopyrite was performed using a Cameca IMS 1280 and a Cameca NanoSIMS 50 ion probes at the Centre for Microscopy, Characterisation and Analysis (University of Western Australia). $^{32}$S, $^{75}$As and $^{197}$Au maps were collected with the Cameca 1280 and $^{197}$Au, $^{34}$S, $^{54}$Fe$^{32}$S, $^{75}$As and $^{60}$Ni$^{32}$S maps were collected with the NanoSIMS.

2.2.7. **Maia detector array and X-ray fluorescence microscopy imaging**

The X-ray fluorescence (XRF) mapping provides quantitative multi-element images. The analyses were performed on the XFM beamline at the Australian Synchrotron with a Maia 384 detector array. The Maia XFM full spectral data were analysed using the GeoPIXE software suite. Please note that chapter IV is dedicated to the development of this technique, applied to ore deposits.

3. **Organisation of thesis**

3.1. **Thesis by papers and authorship**

This thesis is presented as a series of papers; At the time of submission of this thesis, five manuscript have been peer-reviewed and accepted for publication in the journals *Economic Geology* (Chapter II), *Terra Nova* (Chapter III), *Mineralium Deposita* (Chapter IV), *Geochemica and Cosmochemica Acta* (Chapter V) and *Ore Geology Reviews* (Appendix II). This is in accordance with the regulations of the Graduate Research School at UWA. Each chapter is formatted to meet respective Journal requirements.
In chapter II, detailed field work and associated petrography is documented in order to constrain the architecture, structural evolution, timing of mineralisation and ore shoot controls of the Obuasi deposit. Chapter III addresses the question of how arsenopyrite behaves under high strain deformation and wall rock recrystallisation, which leads to a novel interpretation of the common relationship between arsenopyrite and gold deposits. Chapter IV provides the methodology and capabilities of the application of XFM synchrotron elemental mapping to mineral deposit studies. Chapter V documents the evidence for gold remobilisation from the gold-bearing arsenopyrites during metasomatism using detailed texture overprinting relationships and both the XFM synchrotron and NanoSIMS element mapping techniques. Chapter VI summarises the key messages of the thesis and their implication for exploration.

3.1.1. Chapter II

Chapter II is titled “Evidence for Two Stages of Mineralization in West Africa’s Largest Gold Deposit: Obuasi, Ghana” and was accepted for publication in the journal *Economic Geology* (04/06/15). It will be published in the Special Issue on the West African Craton. The paper is first authored by Denis Fougerouse and co-authored by Steven Micklethwaite, Stanislav Ulrich, John Miller, Belinda Godel, David Adams and Campbell McCuaig. Fougerouse was the main scientific investigator and author of the paper. Micklethwaite, Ulrich, Miller and McCuaig played a critical role during the field data collection, interpretations and manuscript redaction. Godel and Adams supervised the data collection and reduction of the high-resolution X-ray computed tomography and microprobe analyses, respectively.

3.1.2. Chapter III

Chapter III is titled “The golden ark: Arsenopyrite crystal plasticity and the retention of gold through high strain and metamorphism” and was accepted for publication in the journal *Terra Nova* (31/01/16). The paper is first authored by Denis Fougerouse and co-authored by Steven Micklethwaite, Angela Halfpenny, Steven reddy, John Cliff, Laure Martin, matt Kilburn, Paul Guagliardo and Stanislav Ulrich. Fougerouse was the main scientific investigator and author of the paper. Micklethwaite played a critical role in the interpretation and manuscript redaction. Halfpenny supervised the Electron backscattered Diffraction (EBSD) data collection and reduction and her input was decisive in the final interpretation. Cliff and Martin supervised the ion probe (SIMS) elemental imaging. Ulrich considerably improved the manuscript during its redaction.
3.1.3. Chapter IV

Chapter IV is titled “Quantified, multi-scale X-ray fluorescence element mapping using the Maia detector array: application to mineral deposit studies” and is published in the journal *Mineralium Deposita*. The paper is first authored by Louise Fisher and co-authored by Denis Fougerouse, James Cleverley, Christopher Ryan, Steven Micklethwaite, Angela Halfpenny, Robert Hough, Mary Gee, David Paterson, Daryl Howard and Kathryn Spiers. Fisher was the main author of the paper. Fougerouse played a critical role in writing the manuscript, figure drafting and data collection, as well as the designing of the structure of the paper. Cleverly, Ryan, Micklethwaite, Halfpenny, Hough, Gee, Paterson, Howard and Spiers helped with the data collection and technical aspect of the complex synchrotron analyses.

3.1.4. Chapter V

Chapter V is titled “Gold remobilisation and formation of high grade ore shoots driven by dissolution-reprecipitation replacement and Ni substitution into auriferous arsenopyrite” and has been accepted for publication in the journal *Geochimica and Cosmochimica Acta* (29/01/16). The paper is first authored by Denis Fougerouse and co-authored by Steven Micklethwaite, Andrew Tomkins Louise Fisher, Yuan Mei, Matt Kilburn, Paul Guagliardo, Angela Halfpenny, Mary Gee, David Paterson and Daryl Howard. Fougerouse was the main scientific investigator and author of the paper. Micklethwaite and Tomkins played a critical role in the interpretation and manuscript redaction. Yuan provided fluid-rock reaction calculations for the mineral replacement reactions and fluid solubilities. Fisher, Gee, Paterson and Howard supervised the data collection and reduction for the XFM synchrotron data. Kilburn and Guagliardo supervised the NanoSIMS data collection and processing. Halfpenny supervised the EBSD data collection and reduction.

3.1.5. Chapter VI

In Chapter VI, we summarise the main outcomes of the above chapters. Although the final report to the sponsor of this study could not be included in this thesis, due to the confidentiality agreement with AngloGold Ashanti, we give an insight of the main exploration outcomes, otherwise reported in details in the final report.
Chapter I: Introduction

3.2. Appendixes

Further petrographic descriptions (appendix I) and supporting references (see below) are also attached as appendixes at the end of the thesis. Appendix II corresponds to a peer-reviewed short paper accepted for Ore Geology Reviews special edition: Mineral Atlas of West Africa.

3.3. Supporting references

3.3.1. Appendix II


3.3.2. Appendix III


3.3.3. Appendix IV


3.3.4. Appendix V


3.3.5. Appendix VI

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3.3.6. Appendix VII


3.4. Summary declaration

I declare that I am responsible for all portions of this thesis, except for collaborative work as acknowledged above. I have not presented any material included in this thesis for a degree at any other university.

4. References


Chapter I: Introduction


Chapter I: Introduction


Wilson, I., 1972, Geochemistry of alteration at the Ashanti mine, University of Leeds, p. 254.


Chapter II: Evidence for Two Stages of Mineralization in West Africa’s Largest Gold Deposit: Obuasi, Ghana

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Chapter II: Multistage mineralization
Chapter II: Multistage mineralization

1. **Abstract**

   The supergiant Obuasi gold deposit is the largest deposit in the Paleoproterozoic Birimian terranes of West Africa with 62 Moz of gold (past production + resources). The deposit is hosted in the Paleoproterozoic Kumasi Group sedimentary rocks composed of carbonaceous phyllites, slates, psammites, and volcaniclastic rocks intruded by different generations of felsic dykes and granites. A three-stage deformation history is defined for the district. The D1\textsubscript{Ob} stage is weakly recorded in the sedimentary rocks as a layer-parallel fabric and indicates bedding parallel shearing occurred during the early stage of deformation at Obuasi. The D2\textsubscript{Ob} is the main deformation stage affecting the Obuasi district and corresponds to a NW-SE shortening. Tight to isoclinal folding, as well as intense sub-horizontal stretching, occurred during D2\textsubscript{Ob}, parallel with the plane of a pervasive NE-striking subvertical foliation (S2\textsubscript{Ob}). Finally, a N-S shortening event (D3\textsubscript{Ob}) refolded previously formed structures and formed a distinct ENE-striking, variably dipping S3\textsubscript{Ob} cleavage that is domainal in nature throughout the deposit. Two economic styles of mineralization occur at Obuasi and contribute equally to the gold budget. These are; (1) gold-bearing sulfides, dominantly arsenopyrite, mainly disseminated in metasedimentary rocks and (2) native gold hosted in quartz veins that are as much as 25 m wide. Microstructural evidence, such as strain shadows surrounding gold-bearing arsenopyrite parallel with S2\textsubscript{Ob} but folded by S3\textsubscript{Ob}, indicates that the sulfides were formed during D2\textsubscript{Ob}. Concentrations of as much as 700 ppm Au are present in the epitaxial growth zones of the arsenopyrite grains. Although the large mineralized quartz veins are boudinaged and refolded (indicating their formation during D2\textsubscript{Ob}) field and microanalytical observations demonstrate that the gold in the veins is hosted in microcracks controlled by D3\textsubscript{Ob}, where the S3\textsubscript{Ob} cleavage crosscuts the quartz veins in the main ore zones. Thus, these observations constitute the first evidence for multiple stages of gold deposition at the Obuasi deposit.

   Furthermore, three-dimensional modelling of stratigraphy, structure, and gold orebodies highlights three major controls on oreshoot location, which are (1) contacts between volcaniclastic units and pre-D1 felsic dikes, (2) fault intersections, and (3) F3\textsubscript{Ob} fold hinges. The maximum age for the older disseminated gold event is given by the age of the granites at 2105 ± 2 Ma, which is within error of hydrothermal rutile in the granites of 2098 ± 7 Ma; the absolute age of the younger gold event is not known.
Chapter II: Multistage mineralization

2. Introduction

The Obuasi deposit is the largest gold deposit hosted in the Birimian of West Africa (Fig. 1). The cumulative past production and resources total 62 Moz of gold as of 2014 (AngloGold-Ashanti, 2014), hosted in both gold-bearing sulfides disseminated in metasedimentary rocks and visible gold in large quartz veins. Although there have been a number of studies of the Obuasi deposit (Junner, 1932; Wilson, 1972; Amanor, 1979; Gyapong, 1980; Bowell et al., 1990; Schwartz et al., 1992; Blenkinsop et al., 1994; Bowell, 1994; Höhndorf et al., 1994; Oberthür et al., 1994; Klemd et al., 1996; Mumm et al., 1997; Oberthür et al., 1997; Yao and Robb, 2000; Yao et al., 2001; Allibone et al., 2002b), there remain two contrasting interpretations on the timing of mineralization at Obuasi based on careful documentation of the geology of the deposit.

The first model, based on petrological and structural observations, proposed that the two contrasting types of mineralization, the gold-quartz veins and auriferous disseminated sulfide ores, can be explained by the system evolving progressively during a single event from ductile to brittle deformation (Blenkinsop et al., 1994; Oberthür et al., 1994). The second model, based mainly on regional, open pit, and underground mapping and detailed field observations, described a multiphase deformation history, but attributed the majority of mineralization in both the veins and the wallrocks to late sinistral reactivation of an earlier fault system (Allibone et al., 2002b).

This paper focuses specifically on re-examining the relative timing of mineralization at Obuasi as part of a larger study to determine the controls on the genesis, location, and geometry of the gold mineralization. Timing of mineralization is critical to understanding oreshoot controls with respect to the structural sequence in order to be able to define an exploration strategy. This study provides analysis of existing and new field data made available by more than ten years of additional mine development since the last study (Allibone et al., 2002b). We present observations integrated across different scales, derived from structural field mapping, deformation fabrics, ore mineralogy, and alteration petrography. Microanalytical techniques employed include scanning electron microscopy (SEM), electron microprobe measurements, and high-resolution X-ray computed tomography. In the first part of the paper, we develop a structural framework and reassess the previous structural models (Blenkinsop et al., 1994; Allibone et al., 2002b). In the second part, we examine the timing of mineralization using the developed structural framework. We finally discuss the significance of our results in a broader context by comparing Obuasi with new regional studies in West Africa (Miller et al., this volume) and other giant gold deposits worldwide.
3. **Geological Background**

West African basement rocks consist of the following main lithostratigraphic units (oldest to youngest): a) high-grade basement gneisses of the Archean Man-Leo shield; b) Paleoproterozoic Birimian volcanic greenstone belts (Sefwi Group); c) Paleoproterozoic Birimian volcano-sedimentary rocks (Kumasi Group), in which the Obuasi deposit is hosted; and d) Paleoproterozoic Tarkwaian Group metasedimentary rocks composed of sandstone and conglomerates (Pigois et al., 2003). Several generations of granitoids intrude these rocks (Fig. 1 and 2; Junner, 1935; Leube and Hirdes, 1986; Leube et al., 1990; Allibone et al., 2002). The oldest rocks in the Obuasi region of southwestern Ghana consist of the Sefwi Group volcanic rocks, which comprise metabasalts, mafic volcaniclastic rocks and rhyolites, and the synchronous tonalite-trondhjemite-granodiorite (TTG) suites of “belt type granitoids” that were emplaced between 2187 and 2158 Ma (Perrouty et al., 2012). This first Paleoproterozoic deformation is referred to as the Eoeburnean (Perrouty et al., 2012) or Eburnean I (Allibone et al., 2002b; Feybesse et al., 2006) orogenic cycle and was followed by a period of regional extension, basin opening, and deposition of sediments of the Kumasi Group. The Kumasi Group rocks include carbonaceous phyllites, greywakes, slates, psammites and volcano-sedimentary rocks in the Obuasi district, deposited between 2157 and 2125 Ma (Davis et al., 1994; Oberthür et al., 1998; Adadey et al., 2009; Perrouty et al., 2012), with detrital zircon U-Pb ages of 2155 ± 2 Ma, which constrains the maximum depositional age (Davis et al., 1994; Oberthür et al., 1998).

The basinal sedimentary rocks of the Kumasi Group were inverted, metamorphosed to greenschist and amphibolite facies (John et al., 1999), and intruded by granitic to granodioritic rocks (“basin type granitoids”), between 2105 ± 2 Ma and 2097 ± 2 Ma in southwestern Ghana, during what is referred to as the Eburnean (Perrouty et al., 2012) or Eburnean II (Allibone et al., 2002b) orogenic cycle. Craton-wide, this cycle spanned the period from 2125 to 1980 Ma (Perrouty et al., 2012). Deformation events discussed in this article all occurred during the younger Eburnean orogenic cycle. Tarkwaian Group rocks could be as young as 2107 Ma (Pigois et al., 2003; Perrouty et al., 2012) and were probably derived from Birimian sedimentary rocks and TTGs uplifted early in the Eburnean II orogenic cycle.

Obuasi, which means “under the rock” in the local Tchi language, is the largest gold deposit discovered in the Obuasi district. Artisanal gold mining at Obuasi has a long history, with the local gold seekers, the Galamsey, panning and digging the quartz veins cropping out at the surface since before the 15th century. Industrial mining officially started in 1897 with the establishment of the Ashanti Goldfields Corporation. To date, 20 individual ore shoots have been found distributed along the 8 km strike length of the deposit; some
reaching depths of >1.6 km, which is the deepest level of mining. More than 15 satellite deposits, defining the Obuasi district, are located within parallel trends west and east of the Obuasi deposit and show a range of different styles of mineralization (Fig. 1 and Allibone et al., 2002).

The Obuasi district is located in the Kumasi volcano-sedimentary basin, in rocks of the Kumasi Group close to the contact with the Ashanti greenstone belt, which itself comprises rocks of the Sefwi Group. The district is located near a concealed intersection between two major faults, the Ashanti and Akropong thrust faults (Perrouty et al., 2012).

Rocks of the Kumasi Group in the Obuasi district most likely represent a metamorphosed turbiditic sequence (Junner, 1932; Amanor, 1979; Gyapong, 1980; Oberthür et al., 1994). Layers of hard, greenish volcano-sedimentary rocks are commonly present adjacent to the mineralized zones. The eastern margin of the Obuasi deposit is bordered by a sliver of mafic volcanic and volcanioclastic rocks probably from the Sefwi Group (Fig. 3; Allibone et al., 2002). Unmineralized and unmetamorphosed dolerite dikes crosscut the ore zone.

In this study, we define the Ashanti fault system as the network of structures and ore shoots in the Obuasi deposit that reaches a maximum of 700 m in width and is locally classified into discrete highly mineralized sub-structures (called ‘fissures’ in Obuasi mining terminology), consisting of multiple strands of graphite-rich shear zones (Fig. 3). Carbon isotope analyses of the graphite contained in the shear zones indicate a sedimentary origin for the carbon (Oberthür et al., 1994). These shear zones bound the mineralization, anastomosing and bifurcating along strike and depth. The most highly endowed graphite-rich shear zones in the Ashanti fault system are named the Obuasi, Main Reef, Ashanti, Côte d’Or, Insintsium, lode 3, and Big Blow shear zones.

In and adjacent to each mineralized shear zone, two styles of mineralization coexist; gold-bearing sulfides, dominantly arsenopyrite, that are disseminated in the metasedimentary host rocks and native gold in quartz veins (Oberthür et al., 1994). The gold-bearing sulfides account for approximately 60% of the gold production at Obuasi (Milési et al., 1991). Commonly, the steeply dipping ore zones, which are as much as 50 m wide, comprise one or several thick mineralized quartz veins and sulfide ores disseminated between two graphitic shears. The sedimentary bedding is tightly folded and several generations of structural fabric can be observed (Blenkinsop et al., 1994; Allibone et al., 2002b).

Two other mineralized trends in the Obuasi district, located west and east of the Obuasi deposit, share the same strike as the Ashanti fault system (Fig. 1). The Binsere trend, located 5 km to the west, contains granite-hosted deposits, whereas mineralization in the eastern Gyabunsu trend is hosted in metasedimentary rocks. The mineralization in the Binsere trend is predominantly contained in gold-bearing sulfides and gold-rich quartz veins, confined to hydrothermally altered granites and their adjacent metasedimentary rocks (Anyankyerim,
Kunka, Yaw Mensakrom, and Nyhiaso deposits: Allibone et al., 2002). The U-Pb zircon ages for intrusions of 2105 ± 2 Ma, as well as Pb-Pb dates on hydrothermal rutile from the Yaw Mensakrom deposit at 2098 ± 7 Ma, provide constraints on the mineralization age in the Binsere trend (Oberthür et al., 1998). In the Gyabunsu trend, located 2 km to the East of the Obuasi deposit, the host rocks are metasedimentary slates and carbonaceous phyllites, interlayered with volcaniclastic rocks. The main gold occurrences are located in the Gyabunsu, Sibi, and Zaks open pits. The mineralization in the Gyabunsu trend is mainly composed of gold-bearing sulfides, with only rare visible gold in boudinaged quartz veins and breccias. The average ore grades in deposits of the Binsere and Gyabunsu trends (5.64 Mt at 2.38 g/t and 0.38 Mt 3.92 g/t respectively) are lower than that of the Obuasi deposit, which can average up to 21.65 g/t in some mining blocks and has an overall resource of 159.89 Mt at 5.32 g/t, containing a total of 27.26 Moz of gold (AngloGold-Ashanti, 2014). Notwithstanding their lower grades, the Binsere and Gyabunsu trends still constitute an important ore resource in the district (Allibone et al., 2002b).
Fig. 1. a) Schematic overview of the geology of the southern part of the West African craton. Position of figure 1b is indicated; b) Simplified Birimian geology of Ghana with alternating greenstone belts and sedimentary basins. Obuasi is located in the Kumasi volcano-sedimentary basin, close to the contact with the Ashanti belt in the vicinity of an intersection between two major faults, the Akropong and Ashanti faults; c) Obuasi district geology. The Binsere and Gyabunsu trends and the main Obuasi deposit share the same strike (modified from Allibone et al. 2012). Position of cross section A-A’ and long section B-B’ (Fig. 6) are indicated. Cross section A-A’ shows one possible interpretation of the structural architecture of the district. The location of figure 3 is indicated on the cross section.
Fig. 2. Simplified stratigraphic column of the Ashanti belt.
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Fig. 3. Schematic cross section through KMS shaft (see Figure 6 long section for location). Several mineralized graphite-rich shear zones (called “fissures” in Obuasi mining terms) anastomose and bifurcate at depth. Lenses of volcaniclastic and mafic rocks are present influencing the geometry of the shear zones (Allibone et al., 2002).
4. Methods

4.1. Field observations, mapping and sample collection

Open pit exposures in each trend in the district (Anyankyerim pit for the Binsere trend, Sibi pit for the Gyabunsu trend, Coral Snake-Anyinam-Big Blow and Sansu pits for the Obuasi deposit) and underground exposures at the Obuasi deposit were studied and mapped in detail. Underground exposures were selected on the basis of discussions with mine geologists, as well as from interpretation of three-dimensional (3D) Leapfrog modelling of the resource wireframe and the drill core database. Mapped areas were also influenced by safety considerations and the availability of active headings. Most active areas of the mine were studied including the Block 1, Block 2, Block 5, Block 8, Block 9, Block 10, the Sansu North Block, and the Upper Mine (located on the Ashanti ‘Fissure’). Both fabric form line and lithological boundary mapping techniques were followed, using aerial photographs as base maps of the open pits and geotechnical surveys when underground. Structural orientations are reported as “dip/dip direction” for planar structures and as “plunge-trend” for linear structures. Data are plotted on lower hemisphere Schmidt projections. The number of data points is reported using the prefix ‘n’.

On the basis of the field observation, 224 samples were collected from outcrop, underground exposure, and drill core, in order to provide a representative database of fault rocks, fabrics, alteration, and ore zones. Geotechnical drill holes were used to collect representative least altered samples distal to the mineralization.

4.2. Petrography and microchemical analysis

Strain fabric characterization, mineral identification, mineral chemistry zonation, overprinting relationships, and paragenesis were investigated with optical techniques and scanning electron microscopy (SEM). Backscattered electron images were generated using a TESCAN VEGA3 SEM. Energy Dispersive X-ray spectra (EDX) were acquired using an Oxford instruments X-Max 50 silicon drift detector with AZtec software fitted on the TESCAN VEGA3. Analytical conditions were 15 kV accelerating voltage with a 1.5 nA probe current.

A JEOL JXA-8530F field-emission gun hyperprobe (electron probe microanalyzer - EPMA) was used for microchemical characterization of gold-bearing arsenopyrite grains. Analyses were performed using the five wavelength dispersive spectrometers. Gold was analyzed simultaneously on two spectrometers, which were integrated to improve the detection limit. Peak count times for all elements analyzed (S, Fe, As, Au) were 160 seconds
per element per spectrometer. Analytical conditions were 20 kV accelerating voltage, 50 nA probe current, and a point beam. During these analyses, we determined the detection limits to be approximately 230 ppm Au in the arsenopyrite grains.

4.3. **High resolution X-ray computed tomography**

To investigate the 3D distribution and geometric relationships of the native gold in the quartz veins, a 25 mm core of a high-grade quartz sample was scanned using the XRADIA Versa XRM 500 3D X-ray microscope, installed at the Australian Resource Research Centre (CSIRO, Kensington, Western Australia). The instrument was operated at 160 kV accelerating potential and 62 mA current and obtained a voxel size of 13.0 µm. A total of 2000 projections were recorded over 360° and were used to reconstruct a three-dimensional volume. The data were processed according to the method of Godel et al. (2013).

5. **Structure, Fabrics, and Deformation History of the Obuasi District**

This section presents descriptions of the fabrics and overprinting relationships in the Obuasi district, and particularly at the Obuasi deposit, in order to describe a framework by which the timing of mineralization can be established. Multiple deformation fabrics of varying intensity and folding, as well as multiple vein generations, are present in the Obuasi district. A complex structural sequence has been recognized, and two slightly different schemes have been previously proposed (Blenkinsop et al., 1994; Allibone et al., 2002b). In the following section, the subscript “Ob” is used to describe the fabrics observed in the Obuasi district during this present study, whereas the subscripts “Al” and “Bl” are used to refer to the fabrics observed by Allibone et al. (2002) and Blenkinsop et al. (1994) (table 3). We use the scheme of Passchier and Trouw (2005) to describe the fabrics. Foliations are classified as either continuous cleavage, when describing rocks with platy minerals that share the same orientation and are closely spaced, or spaced cleavage to describe rocks composed of the repetitive succession of cleavage domains and microlithons. Crenulation cleavage consists of spaced cleavage that preserves older, microfolded fabrics in its microlithons.

5.1. **Early fabrics S0-S1<sub>ob</sub>**

The bedding (S0) in the metaturbidite sequence is defined by alternating layers of dark colored, fine-grained and light colored, coarse-grained sedimentary rocks (Fig. 4a). Facing
and younging directions were mapped and shown to change rapidly over short distances of <10 m, indicating tight internal folding of the lithologies. The bedding typically dips steeply northwest to southeast and the distribution of the bedding orientations plotted on a stereonet describes a weak girdle consistent with folding of the lithology (Fig. 5).

The oldest secondary foliation ($S_{1\text{Ob}}$) corresponds to a low angle or bedding parallel cleavage that is rarely preserved. The few existing measurements of $S_{1\text{Ob}}$ orientation are preserved within hinges of upright tight $F_2$ folds.

5.2. Dominant fabric $S_{2\text{Ob}}$ and sub-horizontal stretching

The dominant foliation ($S_{2\text{Ob}}$) is a continuous cleavage at the micron scale defined by fine-grained, elongate muscovite and quartz grains. In the Obuasi district, $S_{2\text{Ob}}$ strikes northeast and dips subvertically, with dip directions varying from southeast to northwest (Fig. 5). The $S_{2\text{Ob}}$ cleavage is parallel to the fold axial planes of gently plunging tight to isoclinal folds. The $F_{2\text{Ob}}$ folds plunge dominantly toward the northeast, but southwest plunges also occur, indicating these folds are either non-cylindrical and thus doubly-plunging, or underwent post-$F_{2\text{Ob}}$ modification. The $S_{2\text{Ob}}$ overprints both bedding (Fig. 4a) and $S_{1\text{Ob}}$, and in places $S_{2\text{Ob}}$ entirely transposes the earlier fabrics. The $S_{2\text{Ob}}$ cleavage is very consistent across the district.

At the district scale, an intense stretching occurred during the development of $S_{2\text{Ob}}$ (Blenkinsop et al., 1994). Stretching occurs across all three mineralized trends and is preserved in the form of symmetric boudinage of mineralized and unmineralized quartz veins and igneous dikes, as well as symmetric strain shadows surrounding sulfide grains (Fig. 4 and 8). The plunge direction of the boudin necks is relatively consistent in the Anyankyerim (steep NE-plunging boudins) and Gyabunsu (steep SE-plunging boudins) trends (Fig. 4f). Most boudin necks are sub-vertical indicating a sub-horizontal stretching.

In the Obuasi deposit, the stretch is recorded by both boudinaged quartz veins on the macroscopic scale and symmetric quartz strain shadows surrounding porphyroblasts on the microscopic scale. The orientation of the strain shadows surrounding porphyroblasts also indicates sub-horizontal stretching, and this was checked in sections cut orthogonal and parallel to the foliation. Pinch-and-swell features and boudinage are common (Fig. 4c), and mullion structures (Blenkinsop et al., 1994; Goscombe et al., 2004; Fossen, 2010) can also be observed, although at the Obuasi deposit their significance is poorly understood. Depending on the width of the quartz vein, the spacing of the boudin necks is variable from tens of centimeters to tens of meters and no systematic wavelength could be measured. Earlier generations of porphyroblasts of carbonate and sulfide grains are associated with the
development of quartz strain shadows. The axial planes of the strain shadows are parallel to the S2<sub>ob</sub> cleavage and are crenulated by subsequent S3<sub>ob</sub> crenulation cleavage (Fig. 8a, b and d). The majority of strain shadows are symmetric implying bulk pure shear. The only asymmetric strain shadows present indicate opposing movement directions relative to one another and therefore remain consistent with pure shear deformation on the thin section scale (Fig. 8c). The orientations of the strain shadows indicate subhorizontal stretching (λ1) parallel with the S2<sub>ob</sub> cleavage.

In the Anyankyerem deposit along the Binsere trend, granite dikes and sills intruding subvertical bedding are homogeneously altered to quartz, sericite, and carbonates (Yao and Robb, 2000), and are boudinaged. The mineralization style differs from the Obuasi deposit, and is expressed by dikes cut by a generation of quartz veins (Fig. 4d), containing gold-bearing sulfides and rare visible gold. These veins are sub-vertical, striking W-E to NW-SE, intensely developed in the subvertical boudin neck regions of the sills and dikes but folded by later fabric. The mineralized veins are therefore interpreted to have formed during boudinage. Boudinage of the quartz vein arrays in the Obuasi deposit and the granite dikes in Anyankyerem is consistent with a subhorizontal stretching direction (λ1) trending NNE-SSW, which is parallel to the S2<sub>ob</sub> cleavage.

Finally, a critical observation is that the majority of shear zones and faults across the Obuasi district share the same orientation as S2<sub>ob</sub>. They are sub-parallel to the margin of the volcanic belts and sedimentary basins (Fig. 1).

5.3. Late crenulation fabric S3<sub>ob</sub>

A late spaced foliation (S3<sub>ob</sub>) overprints the earlier fabrics and defines a crenulation cleavage (Passchier and Trouw, 2005). The cleavage domains are defined by concentrations of graphite particles, whereas the microlithons preserve the primary rock mineralogy (i.e., muscovite, quartz, and carbonates) and older S2<sub>ob</sub> and S0 foliations. The cleavage domains are smooth, representing a volume of 1 to 5% and a spacing of approximately 100 to 200 µm. The cleavage is parallel and the transition between cleavage domains and microlithons is discrete.

The S3<sub>ob</sub> cleavage has the same orientation as the axial plane of F3<sub>ob</sub> folds and cuts across all previous fabrics (Fig. 4b, 8). The F3<sub>ob</sub> folds are asymmetric and they plunge 20 to 50° to the northeast, whereas the orientation of S3<sub>ob</sub> varies across the Obuasi district (striking ENE-WSW to E-W and dipping 20-60°; Fig. 5). The S3<sub>ob</sub> cleavage shows spatially, as well as lithologically controlled strain partitioning, thus leaving some domains and lithologies undeformed (Blenkinsop et al., 1994; Allibone et al., 2002b). The S3<sub>ob</sub> is better
developed in fine-grained phyllites and does not appear to be present in the greywackes and volcaniclastic rocks. A common intersection lineation is developed between S2\textsubscript{Ob} and S3\textsubscript{Ob} and proved to be a useful identifier of the later cleavage. In contrast to S2\textsubscript{Ob}, no major faults share the same orientation as S3\textsubscript{Ob}.

5.4. **Quartz vein populations**

Various quartz vein generations and orientations are present across the Obuasi district and within the Obuasi deposit. There are quartz (± carbonates) vein populations parallel with S0, S2\textsubscript{Ob}, and S3\textsubscript{Ob}. Less commonly, subvertical veins perpendicular to S2\textsubscript{Ob}, and subhorizontal folded veins can be observed in the Obuasi and Anyankyerem deposits. These veins range in thickness from millimeters to a few tens of centimeters and it has been reported that all orientations are mineralized to some extent (Blenkinsop et al., 1994). Late barren quartz veins with various textures and orientations, from en-echelon steep to flat-lying veins, cross cut all structures.

In this study, we focus on a population of thick quartz veins closely associated with graphite-rich shears at the boundaries of the ore zone. These veins, or quartz lodes, are restricted to the Obuasi deposit, attaining widths of as much as 25 m when two or more graphitic shears intersect. Commonly, the quartz veins strike NE-SW, and thus parallel with S2\textsubscript{Ob}, dip to the west, and are spatially associated with the margins of graphite-rich shear zones. They are deformed into a pinch-and-swell morphology (Blenkinsop et al., 1994), with subvertical and less commonly subhorizontal boudin necks (Fig. 4c, f). These veins contain variable amounts of visible gold, which contribute to local high gold grades, with $>1500$ g/t Au across individual channel samples. The quartz textures can be glassy, milky, or smoky, however only the latter two categories host economic gold grades. The veins internally show crack-and-seal textures, with several sub-parallel laminations of graphite-rich seams. Microstructurally, in the veins, the quartz is entirely recrystallized probably due to subgrain rotation and recrystallization during crystal-plastic deformation (Passchier and Trouw, 2005). Allibone et al. (2002) reported arrays of mineralized sinistral shear veins genetically linked to the thick mineralized quartz veins, however this vein generation was not observed in the currently available exposures throughout the Obuasi mine.
Fig. 4. a) Alternating layers of dark and light lithologies marking the bedding in metaturbidite host rocks. S$_{2\text{Ob}}$ overprints S$_{0\text{Ob}}$; b) S$_{3\text{Ob}}$ crosscut and folds both S$_{2\text{Ob}}$ and S$_{0\text{Ob}}$; c) Boudinaged mineralized quartz vein adjacent to a graphitic shear, underground in the Obuasi Mine (level L39#1, crosscut 86; rock bolts for scale); d) Boudinaged and mineralized dike with subvertical quartz veins and intense quartz veining in the boudin neck area (Anyankyerem Pit, Binsere trend); e) Boudinaged quartz vein in the wall of Sibi pit, Gyabunsu trend; f) Compilation of boudin neck orientations (plunge/azimuth) from quartz veins and dikes across the Obuasi district. The data show the sub-horizontal stretch direction is consistent across the district.
Fig. 5. Stereographic projections of poles to plane for a) the sedimentary bedding (S0); b) S2_{Ob}, and c) S3_{Ob}. The steep bedding is folded dominantly by S2_{Ob} around NE-plunging fold axes. Orientations of moderately dipping S3_{Ob} are more tightly grouped compared to S2_{Ob} orientations.
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5.5. **Summary**

The complexity of the fabric generations in the Obuasi district, and even solely within the Obuasi deposit, has led to the development of two slightly different structural models (Blenkinsop et al., 1994; Allibone et al., 2002b). The new field data and the reassessment of previous data presented here indicate the structures and foliations observed at Obuasi can be depicted in a three-stage sequence.

The sedimentary bedding (S0) is typically very distinct, with alternating layers of darker, fine-grained metapelite and lighter, commonly coarser grained metasandstone. It represents the primary foliation in the district, with younging directions commonly preserved. The oldest secondary foliation (S1ob) recorded in the sedimentary rocks is not well preserved. It has an acute angle with respect to the bedding (S0). The S1ob is folded and transposed by later structures and fabrics (Allibone et al., 2002b).

The dominant secondary foliation in the Obuasi district (S2ob), striking northeast and dipping steeply southeast to northwest, overprints the previously formed (S1ob). The anisotropy introduced by this cleavage possibly influences the geometry of major faults and shear zones in the district, which share the same orientation. The S2ob cleavage is axial planar to and formed coevally with F2ob folds. Subhorizontal stretching occurred during the development of this cleavage, with boudinage of quartz veins and granitic dikes and the formation of quartz pressure shadows surrounding earlier generations of carbonate and sulfide porphyroblasts. Peak metamorphic conditions, calculated after the mineral assemblage of actinolite + chlorite + clinozoisite + quartz + calcite, are estimated to have been 400±50ºC and 2 kbar during the development of this cleavage (Schwartz et al., 1992). This main S2ob cleavage is interpreted to be the result of a NW-SE directed shortening (D2ob). The mineralized thick quartz veins are boudinaged and parallel with S2ob, therefore they must have formed pre- to syn-D2ob. This event corresponds to a period where strain was accommodated by pervasive flattening and stretch, and localized high strain along shear zones.

These fabrics are overprinted by a crenulation cleavage (S3ob), the intensity of which varies across the Obuasi deposit. This spaced crenulation cleavage has a shallow dip to the north-northwest and formed coevally with a second generation of folding (F3ob) plunging 20 to 50º to the northeast. The far-field D3ob shortening direction is NNW-SSE to N-S and is similar to D4Al and D2Al events.

The significance of this structural sequence and how it corresponds with the sequences defined by Blenkinsop et al (1994) and Allibone et al. (2002) is addressed in the later discussion section.
6. Mineralization styles and relative timing of gold deposition at the Obuasi deposit

Exposures within the Obuasi deposit comprise 20 individual ore shoots, distributed along 8 km of strike length and extending for at least 1.6 km below the surface (Fig. 6). More than 15 satellite deposits are located within parallel trends west and east of the main Obuasi deposit (Fig. 1). The ore shoots in the Obuasi deposit contain economic-grade mineralization in two distinct styles;

1. sulfides, predominantly arsenopyrite, with microscopic crystal growth zones containing high gold concentrations,
2. quartz veins with native gold and sulfides.

In this section, we present a description of the overall geometry of the two mineralization styles before examining the geology, mineralogy, texture, and timing of each style relative to the structural sequence.

6.1. Deposit-scale geometry

A long-section projection of ore shoot geometries along the main trend of the deposit is presented in Figure 6. Both mineralization styles are associated with three distinct groups of ore shoots, distinguished on the basis of geometry. These include volcanic rock and dike controlled shoots, shoots associated with fault intersections and bifurcations, and, the most dominant ore shoot group that is associated with F3Ob fold hinges. These geometries were previously identified by Allibone et al. (2002).

The first group of ore shoots correlate with the location of the metavolcanic rocks (Fig. 6). The competency contrast between the hard volcanic units and the more ductile phyllite units is inferred to control the location of the mineralization. The distribution of these units is also interpreted to have had a control on fault propagation through the sequence, as faults commonly form on rheological boundaries. The geometry of the volcanic rocks and dikes reflects the primary intrusive or extrusive geometry and the subsequent deformation overprinting these units. The most remarkable example of this type of ore shoot is the Sansu orebody, associated with the Sansu dike, which cuts through the bedding and is interpreted to form pre- to syn-D1Ob (Allibone et al., 2002). The orebody outcrops at the surface in the Sansu pit. Exploration below the 50 level at a depth of more than 1500 m has not yet reached the base of this mineralization. In the central part of the Obuasi deposit, the Justice ore shoot is also controlled by a volcanic body.

The second group of ore shoots is subhorizontal, plunging steeply to the northeast or shallowly to the south. Our 3D modelling combined with field mapping has identified that
these shoots correspond to anastomosing fault splays, and areas where fault tip bifurcation lines enhance permeability and fluid circulation (e.g. Walsh et al., 1999). Allibone et al. (2002) recognized the same control on these ore shoots. Examples of these ore shoots are the Adansi and Anyinam orebodies (Fig. 6). The largest ore shoot of this type is where the Ashanti and Obuasi shear zones merge.

The third group, which is most dominant group of ore shoots, plunge moderately to the northeast at 20 to 40°. The shoots are consistent with F3Ob fold hinges of the graphite-rich shear zones or the intersection line between the graphite-rich shear zones and the S3Ob cleavage (Blenkinsop et al., 1994; Allibone et al., 2002b; Fougerouse et al., 2013). Although F2Ob and F3Ob both plunge to the northeast, it was possible to discriminate between fold generations using axial plane overprint relationships and confirmed that the ore shoots follow the F3Ob fold hinges. Examples of this type of ore shoot include Coral Snake, ETS, Far North, and SVS (Fig. 6).

6.2. Ore zone-scale geometry

The ore zones commonly dip steeply to the northwest, comprising one or several thick mineralized quartz veins and sulfide-rich ores disseminated between two graphitic shears (Fig. 7). The sulfide ores have increased in their relative economic importance during the past few decades. Their mineralogy is dominated by arsenopyrite, comprising 60-95% of the sulfides, but also with pyrite, pyrrhotite, marcasite, and chalcopyrite, with gold present in the crystal lattice of the sulphides and more rarely as native gold in microcracks in the sulfides (Oberthür et al., 1994).

The thick, mineralized quartz veins sometimes have exceptional gold grades that locally can reach a few percent (Fig. 11a, 12a). Several graphite-rich shear zones and associated thick quartz veins may be present in the same ore zone (Fig. 9) and commonly are given the names West, Central, or Hanging wall lodes. The veins consist of quartz, minor ankerite, sulfides (<1%), and host rock fragments.
Fig. 6. Projected long-section of high-grade ore shoots, underground infrastructure. Steep and sub-horizontal ore shoots coincide with the intersection of faults. In contrast, moderately plunging ore shoots are associated with folding (F30b) of graphitic-rich fault zones (modified from Allibone et al., 2002). Atypical ore shoot geometries are linked to intersection of faults with volcanic units in the stratigraphy. Location of KMS shaft (cross section; Fig. 3), level 22#1 crosscut 275 (Fig. 9), level 43#1 crosscut 169 (Fig. 10) and samples studied for petrography are plotted.
Fig. 7. Schematic cross section through a typical ore zone. The ore zone is often constrained between two graphitic faults with a thick quartz vein typically located on the western side of the ore zone. The proportion of gold-bearing arsenopyrite increases toward the mineralized quartz veins, while the proportion of carbonates increase toward the ore zone.
6.3. Mineralization style I; arsenopyrite-hosted gold mineralization and its relationship to deformation fabrics

The sulphide ores, herein referred to as mineralization style I, represent the refractory ores of the Obuasi mining operations. In this section, we document the mineralogy, chemistry and microstructures of this mineralization style.

The distribution of arsenopyrite decreases away from the thick quartz veins and thus defines an arsenopyrite halo surrounding the veins. In the ore zones, the abundance of arsenopyrite is typically higher in the fine-grained psammite than in the greywacke (Fig. 7).

The SEM images and EPMA analyses revealed zoning of the larger arsenopyrite grains with multiple zones of gold enriched rims and typically gold-poor cores (Fig. 8d). Gold concentration in the rims can reach as high as 700 ppm, whereas concentrations in the cores are below the detection limit of 230 ppm (Table 1). This observation confirms SIMS (Secondary Ion Mass Spectrometer) analyses and interpretations from previous studies (Oberthür et al., 1994; Oberthür et al., 1997). No micronuggets or gold particles were observed at the micron scale in the arsenopyrite grains, except rarely in cross-cutting microcracks, so almost all gold must be present in solid solution or as nanoparticles. Along grain boundaries, there are small, spatially restricted zones in the arsenopyrite grains characterized by brighter backscatter in SEM photomicrographs, indicating a higher than average atomic mass (Fig. 8d; Morey et al., 2008). In these zones, gold concentrations are below detection limit, whereas arsenic concentrations are higher and sulfur content lower relative to the remainder of the arsenopyrite rims. Following the description of Morey et al. (2008), these zones are considered to be the result of alteration and chemical modification.

Petrography and microstructural studies show that a large proportion (80 to 90%) of the gold-bearing arsenopyrite grains disseminated in the sedimentary rocks are aligned with S2Ob. Approximately 50% of these gold-bearing sulfides are associated with quartz strain shadows also parallel with S2Ob, which are reworked and crenulated by the S3Ob crenulation cleavage (Fig. 8a, b and d). Typically, arsenopyrite grains have only have weak strain caps on their margins orthogonal to the strain shadows, consistent with crystallization occurring synchronous with D2Ob (Passchier and Trouw, 2005). The strain shadow orientation is concordant with the D2Ob subhorizontal stretching. It is important to note that some samples do not show strain shadows surrounding sulfides and only weakly developed fabrics. A number of these samples are grains hosted by the coarser grained sedimentary rocks, reflecting a lithological control rather than a difference in timing. Notwithstanding this, Allibone et al. (2002) reported large needles of arsenopyrite overprinting the latest cleavage (S3Ob), indicating formation during a later event. However, the scarcity of these larger
arsenopyrite grains suggests that later events were associated with only limited amounts of disseminated sulfide and related gold deposition. The width of the arsenopyrite halo can reach up to 50 m from the thick quartz veins.

In addition to the mineralized arsenopyrite, the metasedimentary rocks preserve a 25 to 50 m wide ankerite and siderite alteration halo from the edges of the arsenopyrite mineralization. Petrography, integrated with field work and systematic sampling demonstrates that the alteration is zoned with an inner halo of arsenopyrite surrounding the quartz veins and an outer halo of carbonates. Both of the carbonate minerals are deformed within the S2\textsubscript{Ob} cleavage and host inclusions of quartz and mica, parallel with the S2\textsubscript{Ob} cleavage, indicating precipitation contemporaneous with development of this cleavage (Fig. 8e, f; cf. Passchier and Trouw, 2005).

**Table 1.** Microprobe analysis of sample DF073(1) in Wt%. BDL refers to “Below Detection Limit” (230 ppm).

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>As</th>
<th>Au</th>
<th>Fe</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>23.309</td>
<td>41.894</td>
<td>BDL</td>
<td>35.859</td>
<td>101.06</td>
</tr>
<tr>
<td>Core</td>
<td>21.995</td>
<td>43.740</td>
<td>BDL</td>
<td>35.190</td>
<td>100.92</td>
</tr>
<tr>
<td>Rim</td>
<td>22.047</td>
<td>43.860</td>
<td>0.06</td>
<td>35.063</td>
<td>101.03</td>
</tr>
<tr>
<td>Rim</td>
<td>22.319</td>
<td>43.901</td>
<td>0.07</td>
<td>35.380</td>
<td>101.67</td>
</tr>
<tr>
<td>Rim</td>
<td>21.558</td>
<td>44.718</td>
<td>0.03</td>
<td>34.979</td>
<td>101.28</td>
</tr>
<tr>
<td>Rim</td>
<td>21.524</td>
<td>44.320</td>
<td>0.06</td>
<td>34.831</td>
<td>100.74</td>
</tr>
<tr>
<td>Alteration zone</td>
<td>20.072</td>
<td>45.444</td>
<td>BDL</td>
<td>33.580</td>
<td>99.10</td>
</tr>
<tr>
<td>Alteration zone</td>
<td>20.752</td>
<td>46.059</td>
<td>BDL</td>
<td>34.730</td>
<td>101.54</td>
</tr>
</tbody>
</table>
Fig. 8. a, b and c) Optical micrograph of gold-bearing arsenopyrites in sedimentary rocks (phyllites). Most of the arsenopyrites have strain shadows aligned with the main pervasive cleavage and refolded by the later spaced cleavage. Their strain caps, developed by the accumulation of cleavage planes against a hard object, are only weakly developed; d) Backscattered image of an arsenopyrite, EPMA gold concentrations are reported up to 700 ppm. BDL refers to “Below Detection Limit” (table 1; sample DF073(1)); e) Backscattered image of siderites and ankerite aligned with the NE-SW cleavage; f) photograph of ankerite aligned with the NE-SW cleavage. Inset shows strain shadows around the ankerite grains parallel to S2Ob and refolded by S3Ob.
6.4. Mineralization style II; visible gold and its relationship to late-stage fracturing and folding

The quartz vein-hosted ores, herein termed mineralization style II, are extremely high grade and characterized by visible gold. In this section, we describe the nature of this mineralization style using observations from underground mapping, SEM data, and X-ray computed tomography.

More than 20 localities were mapped underground in the Obuasi deposit. Two exceptionally high-grade examples are presented in more detail here, from level 22 crosscut 275 and level 43 crosscut 169. The sublevel 22 crosscut 275 (L22#1 XC275) shows a high-grade ore zone aligned with the Sansu ore shoot, plunging 20° to the northeast. The metre wide central quartz vein follows a lithological contact between phyllites and fine-grained greywackes. The vein changes in strike by 20° (Fig. 6, 9) and has extremely high grades at the bend of the vein (3 m at 1750 g/t Au). A calculated $\pi$-axis, corresponding to the fold axis of the folded quartz vein (Fig. 9c), plunges at 17° to the northeast. This orientation is parallel to the orientation of the late F3_Ob folds in the southern part of the deposit developed during D3_Ob. A second, 5 metre wide quartz vein borders the graphitic shear on the western end of the mineralized area with high gold grades, but contains lower grades than the vein in the central zone. In contrast to the very variable distribution of the visible gold mineralization, the gold-bearing arsenopyrite disseminated in the sedimentary rocks is evenly distributed along strike and the arsenopyrite abundance shows no spatial correlation with the folding of the quartz vein. This suggests arsenopyrite precipitation is a distinct event relative to visible gold formation.

Similar observations can be made in other areas of the mine. The sublevel 43 crosscut 169 (L43#1 XC169) was mapped in detail to describe exposures associated with a high-grade quartz vein (Fig. 6, 10). The quartz vein is folded with its measured fold axis parallel to the late F3_Ob folds determined in the north part of the mine in the Anyinam pit. The graphitic faults, bedding, the zone of mineralized arsenopyrite ore (mineralization style I), and the zone of carbonate alteration are folded with the quartz vein. Furthermore, the S3_Ob cleavage can be measured in the metasedimentary rocks and its orientation is parallel with the axial plane of the folded quartz vein. Late gold-bearing fractures, parallel to S3_Ob, also overprint the boudinaged quartz vein suggesting that the fractures and S3_Ob are coeval. The grade control data (Roger Kumi personal communication) show that the gold concentrations in the quartz vein increase progressively toward the fold hinge of the quartz vein (Fig. 10).

The SEM and high-resolution X-ray computed tomography analyses indicate that the gold and accessory minerals are distributed along fracture planes crosscutting the quartz
vein, rather than disseminated throughout the quartz vein (Fig. 11 and 12). The gold particles are flaky with irregular sizes filling the porosity in the quartz created by the fracturing. In the fractures of the quartz veins, native gold is associated with muscovite and small amounts of graphite (<1%), but also galena, chalcopyrite, sphalerite, bournonite, boulangerite, tetrahedrite, aurostibine, löellingite, pyrite, arsenopyrite, and rare bismuth tellurides as accessory minerals (Fig. 11b; Oberthür et al., 1994). The minerals are typically xenomorphic, unfractured and can reach several hundred microns in maximum dimension. The mutual intergrowth of these minerals and gold indicates synchronous deposition (Fig. 11b; Oberthür et al., 1994). This generation of arsenopyrites, associated with native gold in the fractures of the quartz veins, can contain between 0.80 and 2.25 % of gold (Oberthür et al., 1994).

Finally, at the thin-section scale, porphyroblasts of retrograde chlorite grains overprint both the S2Ob and late S3Ob cleavage in the metasedimentary rocks within meters of the mineralized quartz veins (Fig. 11d). The porphyroblasts form large aggregates (>100 μm) and they host inclusions preserving the crenulated fabric observed in the surrounding matrix. The abundance of the overprinting chlorite increases closer to the high-grade ore zones in the quartz veins.
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Fig. 9. Underground geological map of level 22#1 crosscut 275, showing grade distribution. a) The highest gold grades are located in the hinges of the late F3 folds; b) Stereonet shows the mineralized quartz vein is folded with a calculated fold axis ($\pi$-axis) corresponding to F3_{Ob} observed in the south part of the mine.
Fig. 10. Underground geological map of level 43#1 crosscut 169. a) The highest gold grades are located in the hinges of the late F3 folds; b) The mineralized quartz vein is boudinaged and overprinted by late fractures parallel to the late S3_{ob} E-W cleavage; c) Stereonets of structural measurements, the mineralized quartz vein is folded with fold axes corresponding to F3 in the north part of the mine.
Fig. 11. a) Underground exposure of a mineralized ~3 m wide quartz vein; b) example of sulfides associated with the visible gold; c) Backscattered image of gold confined to a fracture network in a quartz vein and concentrated along a microfracture developed within muscovite aggregates, parallel to muscovite cleavage; d) Chlorite porphyroblasts overprinting the late S3_{orb} E-W cleavage.
Fig. 12. a) Hand specimen of quartz hosting visible gold in fractures; b) Isosurfaces showing the 3D gold distribution of gold particles as obtained using high-resolution X-ray computed tomography. Gold fills and defines fracture networks in the quartz vein.
7. **Discussion**

7.1. **Model for structural evolution and multiple episodes of mineralization at Obuasi**

We have established, with respect to the relative timing of mineralization and structural evolution of the Obuasi deposit that: a) the first bedding-parallel fabric $S_{1_{Ob}}$ is only poorly preserved; b) the most dominant fabric, $S_{2_{Ob}}$, is striking northeast, dipping steeply southeast to northwest, and is associated with sub-horizontal stretching; c) strain shadows surrounding gold-bearing arsenopyrite and carbonate grains formed during the development of this cleavage ($S_{2_{Ob}}$) and were then folded during $D_{3_{Ob}}$ (Fig. 13); d) the $S_{3_{Ob}}$ is the last preserved pervasive foliation, striking ENE-WSW to E-W and shallowly dipping to the north-northwest; e) the associated $F_{3_{Ob}}$ fold hinges plunge 20 to 50° to the northeast, refold the mineralized shear zones, and correspond to the dominant high grade ore shoot geometry at the deposit scale (group 3 - Fig. 6); and f) the large mineralized quartz veins are boudinaged during $D_{2_{Ob}}$ and are folded by $F_{3_{Ob}}$ folds, and therefore formed pre- to syn-$D_{2_{Ob}}$, but the gold and accessory sulfides in the veins were introduced during $D_{3_{Ob}}$.

At the underground drive scale, $F_{3_{Ob}}$ fold hinges also correspond to high gold grades and visible gold mineralization (Fig. 9, 10). At the microscopic scale, SEM work and the 3D visualization of the distribution of gold particles in high-grade quartz vein samples using high resolution X-ray computed tomography show that all the visible gold and accessory sulfides are located within microfracture networks overprinting the quartz veins, and that late chlorite in the wallrock is parallel with $S_{3_{Ob}}$. The chlorite porphyroblasts are thus coeval with the fracture-hosted gold ores. We conclude that the gold contained in the crystal lattice of the gold-bearing arsenopyrites and the associated carbonate alteration halo formed syn-$D_{2_{Ob}}$. In contrast, we conclude that the visible gold mineralization and accessory sulfides in the Obuasi veins formed during $D_{3_{Ob}}$ and thus post-dates the formation of the major quartz veins themselves and the sulfide mineralization in the surrounding wallrocks (Table 2; Fig. 14).

The results of this study differ from observations described by Allibone et al. (2002), Oberthür et al. (1994), and Blenkinsop et al. (1994), in providing a new model for the timing of mineralization and structural development. For example, Oberthür et al. (1997) concluded that the refractory disseminated gold and visible gold in the veins were formed as one event, while we interpret the gold to have been formed in two distinct events. Nonetheless, this study also confirms a number of important relationships established by these latter studies (Table 2 and 3). We discuss the similarities and differences in more detail below.
Firstly, $D_{1Ob}$ and $D_{1Al}$ correspond with one another, although this was not reported by Blenkinsop et al. (1994), probably due to poor preservation of the deformation in the rocks. The defined $D_{2Ob}$, $D_{2Al}$ and $D_{1Bl}$ episodes likely represent the same event, where strain was accommodated by pervasive flattening and stretching, and localized high strain along shear zones. The $D_{3Ob}$, $D_{4Al}$ and $D_{2Bl}$ episodes also represent the same structural event, which is characterized by refolding of the shear zones. Allibone et al. (2002) reported a further weakly developed flat-lying ($S_{3Al}$) cleavage striking northeast. However, this cleavage was not observed in this study, nor by Blenkinsop et al. (1994), which may indicate that this cleavage is not a pervasive fabric across the district and is likely the product of localized deformation, rather than a distinct regional tectonic event.

Secondly, with regards to ore shoot controls, the significance of fault intersections and volcanic units was identified by Allibone et al. (2002) and by this study. The ore shoot group controlled by the late folding ($F_{3Ob}$) was identified by all studies, although Blenkinsop et al. (1994) and Oberthür et al. (1994) did not distinguish between fold generations.

**Table 2.** New structural scheme for Obuasi integrating the timing of mineralization; the first gold event occurred during $D_{2Ob}$ and the second during $D_{3Ob}$.

<table>
<thead>
<tr>
<th>DEFORMATION</th>
<th>REPRESENTATIVE STRUCTURES</th>
<th>MINERALIZATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{1Ob}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1 rarely preserved bedding parallel shearing</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Similar to $D_{1Al}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{2Ob}$</td>
<td></td>
<td>First stage mineralization</td>
</tr>
<tr>
<td>NW-SE shortening</td>
<td>Steeply dipping NE striking $S_{2Ob}$</td>
<td>Disseminated gold-bearing sulphides (Apy, Py)</td>
</tr>
<tr>
<td>$F_{2Ob}$ tight to isoclinal folding, Large quartz veins, Sub-horizontal stretching (boudinage, $BN=bou$ in neck)</td>
<td>Similar to $D_{1Bl}$ and $D_{2Bl}$</td>
<td></td>
</tr>
<tr>
<td>$D_{3Ob}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NNW-SSE shortening</td>
<td>Gently dipping E to NE $S_{3Ob}$</td>
<td>Second stage mineralization</td>
</tr>
<tr>
<td>$F_{3Ob} = 30 \rightarrow 45$</td>
<td>Folding of the Ashanti fault</td>
<td>High grade visible gold</td>
</tr>
<tr>
<td>Similar to $D_{2Bl}$ and $D_{4Al}$</td>
<td></td>
<td>(Au, Gn, Ccp, Sp, Brn, Ast...)</td>
</tr>
</tbody>
</table>
Thirdly, with regards to the timing of arsenopyrite growth, Oberthür et al. (1994) reported that the preferred orientation of the gold-bearing arsenopyrite in the wallrocks is commonly parallel to S$_{2\text{ob}}$, which is in agreement with this study. Junner (1932) also documented that the arsenopyrite at Obuasi was fringed by “fibrous quartz” and provided a photomicrograph demonstrating folding of these quartz fringes (Fig. 4 in Junner, 1932). In contrast, Allibone et al. (2002) reported arsenopyrite needles in the wallrocks overprinting the S$_{3\text{ob}}$ cleavage and interpreted the bulk of the sulfide mineralization disseminated in the sediments to post-date D$_{3\text{ob}}$. However, from our analysis, in approximately 50% of thin sections examined from the mineralized wallrocks, 80 to 90% of the arsenopyrite grains have strain shadows developed during D$_{2\text{ob}}$. We also found specimens without strain shadows correlated with coarser grained sedimentary rocks, reflecting a lithological control rather than a difference in timing. As such, we conclude that the timing of the majority of the gold-bearing arsenopyrite disseminated in the wallrocks is syn-D$_{2\text{ob}}$.

Fourthly, Allibone et al. (2002) reported large, mineralized quartz vein arrays that were interpreted to form during late sinistral strike-slip movement on the shear zones (late-D$_{4\text{Al}}$ to D$_{5\text{Al}}$ in Allibone et al., 2002). The sinistral shear vein arrays were attributed to a late event of wrench tectonics operating at brittle-ductile conditions, and post-dating our D$_{3\text{ob}}$ during the main NNW-SSE compression. Conversely, in this study we report thick mineralized quartz veins have been symmetrically boudinaged and dynamically recrystallized, indicating that they were deformed during D$_{2\text{ob}}$ and therefore formed pre- to syn-D$_{2\text{ob}}$. Arrays of sinistral shear veins, as reported by Allibone et al. (2002), were not observed in the highly mineralized ore zones in this study or by Blenkinsop et al. (1994). We suggest the shear vein arrays observed by Allibone et al. (2002) correspond to late, localized sinistral strike-slip movement (e.g., Ashanti fissure), but that such an event is not expressed pervasively across the deposit and reflects a minor control on vein hosted mineralization for the whole deposit.

The Allibone et al. (2002) model attributed the timing of gold mineralization to the late sinistral reactivation of the Ashanti fault system during late-D$_{4\text{Al}}$ to D$_{5\text{Al}}$. This interpretation is based on a) the description of veins showing sinistral kinematics during their formation; b) the orebody geometry with flexure (F$_{3\text{ob}}$) of the shear zones acting as dilational or compressional jogs during strike-slip movement; c) slickenlines on faults and surfaces of veins and; d) acicular arsenopyrite grains overprinting the late S$_{3\text{ob}}$ cleavage.

Converse to Allibone et al. (2002), Oberthür et al. (1994) and Blenkinsop et al. (1994) interpreted the two mineralization styles as the product of a single progressive event during D$_{1\text{Bl}}$/D$_{2\text{Bl}}$, with the varying styles related to deformation occurring under different pressure-temperature-strain rate conditions. Initially the gold-bearing sulfides are introduced in a ductile regime while, as the system evolves, the quartz veins and visible gold are deposited in a more brittle regime. This model is based on a) the chemical association being different
between the two styles of mineralization, with an As-S-Au signature developing initially and a polymetallic signature developing in the later stages; b) sulfidized rock fragments in the quartz veins; and c) the apparent contrast of ductile versus brittle textures.

In contrast to these two models, we summarize the timing of mineralization as follows (Table 2; Fig. 14). First, quartz veins, with gold-bearing sulfides in surrounding wallrocks, formed syn-D\textsubscript{2\text{Ob}}. The sulfides are the product of sulfidation of the wallrock due to a pervasive infiltration of fluid through the metasedimentary rocks. Secondly, stretching of the quartz veins and crystallization of strain shadows surrounding the sulfides occurred later during the D\textsubscript{2\text{Ob}} event. Finally, folding of the quartz veins, and syn-D\textsubscript{3\text{Ob}} precipitation of visible gold with accessory sulfides in fractures, created high-grade ore shoots in fold hinges plus crenulation of the D\textsubscript{2\text{Ob}} strain shadows surrounding sulfide and carbonate grains. Thus, this study reports that economic mineralization in the Obuasi deposit developed during at least two separate structural events. Furthermore, considering the results of Allibone et al. (2002) in the context of this study, a potential third minor mineralizing event may exist in parts of the Obuasi deposit. This event is limited to a small amount of arsenopyrite grains overprinting the S\textsubscript{3\text{Ob}} cleavage and gold veining in localized areas of the Obuasi deposit and district (e.g., Bekansi and Kotopre prospects).
Fig. 13. Interpretation of the evolution of the strain shadows surrounding gold-bearing arsenopyrite and the associated strain ellipsoid; the arsenopyrite grains crystallize during D2\textsubscript{ob} and develop strain shadows during this period. They are later folded during D3\textsubscript{ob}.
Fig. 14. Interpretation through time of the mineralizing events in Obuasi in a schematic underground map. The arsenopyrite mineralization and boudinage of the quartz vein is synchronous with D2_{Ob} and stretching, the visible gold mineralization overprints the quartz vein in the F3_{Ob} fold hinges.
Table 3. Comparison of structural evolution outlined in this study with compilation of previous structural studies of Obuasi (Blenkinsop et al., 1994; Allibone et al., 2002) and regional interpretation (Miller et al., this volume).

<table>
<thead>
<tr>
<th>This study Obuasi</th>
<th>Blenkinsop et al., 1994 Obuasi</th>
<th>Allibone et al., 2002 Obuasi</th>
<th>Miller et al., this volume Ghana</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>D1</strong>&lt;sub&gt;Ob&lt;/sub&gt;</td>
<td><strong>D1</strong>&lt;sub&gt;AI&lt;/sub&gt;</td>
<td><strong>D1</strong>&lt;sub&gt;AI&lt;/sub&gt;</td>
<td><strong>D2</strong>&lt;sub&gt;Ob&lt;/sub&gt;</td>
</tr>
<tr>
<td>S1&lt;sub&gt;Ob&lt;/sub&gt; rarely preserved bedding parallel shearing</td>
<td>S1&lt;sub&gt;AI&lt;/sub&gt; rarely preserved bedding parallel shearing</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>D2</strong>&lt;sub&gt;Ob&lt;/sub&gt;, NW-SE shortening</td>
<td><strong>D2</strong>&lt;sub&gt;AI&lt;/sub&gt;, NW-SE shortening</td>
<td><strong>D2</strong>&lt;sub&gt;AI&lt;/sub&gt;, NW-SE shortening</td>
<td><strong>D3</strong>&lt;sub&gt;Ob&lt;/sub&gt;, NW-SE shortening</td>
</tr>
<tr>
<td>S2&lt;sub&gt;Ob&lt;/sub&gt; steep Easertly dipping NE-SW F2&lt;sub&gt;Ob&lt;/sub&gt; asymmetric folding</td>
<td>Isoclinal folds with axial surface parallel to the regional faults and shear zones</td>
<td>S3&lt;sub&gt;AI&lt;/sub&gt;, subvertical cleavage NE-SW</td>
<td>S3&lt;sub&gt;AI&lt;/sub&gt;, subvertical cleavage NE-SW</td>
</tr>
<tr>
<td>Large quartz veins</td>
<td>Ashanti thrust fault</td>
<td></td>
<td>Thrust faults (Ashanti, Damang, ...)</td>
</tr>
<tr>
<td>NE-SW sub-horizontal stretching and boudinage</td>
<td><strong>D3</strong>&lt;sub&gt;AI&lt;/sub&gt;, NW-SSE shortening</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Gold-bearing sulfide mineralization</strong></td>
<td></td>
<td><strong>D3</strong>&lt;sub&gt;AI&lt;/sub&gt;, NE crenulation cleavage overprinting S2&lt;sub&gt;AI&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td><strong>D3</strong>&lt;sub&gt;Ob&lt;/sub&gt;, NW-SSE shortening</td>
<td><strong>D2</strong>&lt;sub&gt;AI&lt;/sub&gt;, NNE-SSW shortening</td>
<td><strong>D4</strong>&lt;sub&gt;AI&lt;/sub&gt;, NW-SSE shortening</td>
<td><strong>D4</strong>&lt;sub&gt;AI&lt;/sub&gt;, NW-SSE shortening</td>
</tr>
<tr>
<td>S3&lt;sub&gt;Ob&lt;/sub&gt; overprinting cleavage E to NE</td>
<td>S2&lt;sub&gt;AI&lt;/sub&gt; variable orientation (E-W to NW-SSE), gently dipping to the NE</td>
<td>Steeply plunging upright folds (F4&lt;sub&gt;AI&lt;/sub&gt;) developed on the western side of the shear</td>
<td>Sinistral shear reactivation of D3&lt;sub&gt;Ob&lt;/sub&gt; thrust</td>
</tr>
<tr>
<td>Cross cutting folding plunging 50° to 30° to the NE</td>
<td></td>
<td></td>
<td>S4&lt;sub&gt;2AI&lt;/sub&gt;, crenulation cleavage</td>
</tr>
<tr>
<td>Folding of the Ashanti fault</td>
<td></td>
<td></td>
<td>ENE-WSW</td>
</tr>
<tr>
<td><strong>High grade visible gold mineralization</strong></td>
<td></td>
<td></td>
<td>Greenschist retrograde metamorphism</td>
</tr>
</tbody>
</table>

- Indicates data not observed in this study.
7.2. **Evidence for multiple stages of mineralization in the Birimian terrains of West Africa and worldwide**

The Birimian terranes are unusually well-endowed and contain a number of world-class deposits (>6 Moz as defined by Schodde and Hronsky, 2006), including Sadiola, Morilla, Syama, Siguiri, Damang, Prestea, and Tarkwa (e.g. Masur et al., this volume; Lebrun et al., this volume; McFarlane et al., 2011; Perrouty et al., 2012). It has been demonstrated in this study that the Obuasi gold deposit formed mainly during two mineralizing events. Although the two events are distinct, they both likely occurred during the second cycle of the Eburnean orogeny, with the early stage of mineralization constrained by U/Pb zircon ages of the Anyankyerem granite to younger than 2105 ± 2 Ma (Oberthür et al., 1998) and hydrothermal rutile from the Yaw Mensakrom deposit at 2098 ± 7 Ma, while Le Mignot et al. (this volume) reported a Re-Os age of 2040 ± 87 Ma for disseminated gold-bearing arsenopyrite. As such, this raises the question as to whether there is also evidence for multiple episodes of mineralization across the Ashanti belt. In the Ashanti greenstone belt, several economic gold mineralizing events have been described (Parra-Avila et al., In press; Miller et al., This volume). The oldest lode gold event is bracketed at the Wassa/Benso system between 2192.7 ± 4.6 Ma and 2159.5 ± 7.5 Ma (Luis Parra et al., In press) and it has been suggested Wassa-like deposits could represent a possible source for the Tarkwa paleoplasier deposits, such as the 41 Moz Au Tarkwa deposit (Perrouty et al., 2012). The Tarkwa paleoplasier deposit was deformed during the main NW-SE shortening (D2Kr), which is broadly at the same time as the first sulfide mineralization event at Obuasi, indicating that Obuasi is an unlikely source for the detrital gold in the Tarkwaian basin (Milési et al., 1991). Finally, mineralization at the Damang orogenic lode-gold system, which overprints the Tarkwa paleoplasier, has been dated (U/Pb on hydrothermal xenotime) at 2063 ± 9 Ma (Pigois et al., 2003) and consequently represents a late gold episode in the Ashanti belt. In summary, it appears that the West African Birimian terranes have been affected by multiple mineralizing events and a minimum of two, and possibly three, separate events are expressed in the one deposit at Obuasi.

Worldwide, many giant orogenic gold deposits have experienced multiple stages of successive, nevertheless different, mineralization episodes in the same location over time (McCuaig et al., 2001; Bucci et al., 2004; Kolb et al., 2005; Robert et al., 2005; Bateman et al., 2008). By way of example, the giant Western Australia Kalgoorlie gold deposit (consisting of Golden Mile and Mount Charlotte mineralization) contains evidence of at least two mineralizing events. Field relationships indicate that the vein stockwork and associated gold-bearing pyrites in the wall rock of the Mount Charlotte type mineralization,
overprints the shear zone hosted gold of the Golden Mile (native gold and Ag-Au telluride Fimiston and Oroya lodes). Differences between the two styles of mineralization include ore mineral assemblages, wall rock alteration styles, wall rock fabrics, and P-T conditions (Bateman and Hagemann, 2004; Gauthier et al., 2007; Mueller and Muhling, 2013; Mueller, 2014). Bateman and Hagemann (2004) conclude that at least two distinct episodes of mineralization took place in this giant gold deposit, and it has subsequently become clear that these events occurred within a geochronological period of approximately 25 Myrs of each other (Vielreicher et al., 2010).

Other examples of large gold deposits and districts formed by multiple events, include the the Val-d’Or goldfields (Abitibi, Canada: Couture et al., 1994), the Hutti gold deposit (Dharwar craton, India: Kolb et al., 2005), the Red Lake deposit (Ontario Canada: Dubé et al., 2004) and the Bendigo-Ballarat goldfields (central Victoria, Australia: Bierlein et al., 1999; Wilson et al., 2013). In the Val-d’Or goldfields, the deposits have been classified into two categories, “young” undeformed deposits deposited subsequent to 2630 Ma (Sigma, Lamaque, Camflo, Perron, and Béliveau) and “older” polydeformed deposits deposited prior to 2690 Ma (Siscoe, Kiena, Orion, and Norlartic mines), thus demonstrating that at least two distinct major gold mineralizing events occurred there (Couture et al., 1994). The Hutti gold deposit formed during two successive tectonic events with different structural controls, alteration, and ore signatures, at different P-T conditions (Kolb et al., 2005). The early stage is characterized by disseminated mineralization associated with sulfides and the late stage is defined by visible gold in laminated quartz veins (Kolb et al., 2005). At the Red Lake deposit, the high-grade mineralization, comprising arsenopyrite and visible gold, occurred before 2712 Ma and a second, less significant stage of visible gold mineralization occurred after 2702 Ma (U-Pb on zircons; Dubé et al., 2004). The Bendigo-Ballarat goldfields underwent an initial mineralization episode between 460 and 440 Ma (hydrothermally altered whole rock Ar/Ar), followed by a second episode of mineralization between 410 and 380 Ma (Ar/Ar on hydrothermal muscovite separates; Bierlein et al., 1999). Similar to the Obuasi deposit, the Bendigo deposit in the Bendigo-Ballarat goldfields comprises early wall rock disseminated sulphide mineralization and later vein hosted visible gold (Wilson et al., 2013).

The conclusion that multiple events are responsible for gold mineralization in Obuasi and other deposits around the world raises the question, critical for exploration, of whether metal introduced in the first mineralizing event is remobilized, or if new batches of gold are added to the deposits in subsequent mineralizing events. In the Ashanti belt, both potential mechanisms have been invoked. Oberthür et al. (1997) briefly argue that the preserved textures of gold zonation in arsenopyrite suggest remobilization did not occur. In contrast, Mumin et al. (1994) developed a model of gold remobilization from pyrite and arsenopyrite,
for the Bogosu-Prestea mining district, based on gold zonation textures using ion probe and EPMA data.

8. Conclusion

In this study we have identified a three stage structural sequence consisting of $D_{1Ob}$ defined as bedding parallel shearing and only weakly recorded in the rock fabric, the main $D_{2Ob}$ NW-SE shortening event, and, finally, a N-S to NW-SE shortening event ($D_{3Ob}$). Two spatially and temporally distinct styles of mineralization are clearly identified, gold-bearing arsenopyrite that is disseminated in metasedimentary rocks and gold in fractures in thick quartz veins. The gold-rich arsenopyrite ores precipitated synchronously with isoclinal folding, $S_{2Ob}$ foliation development, and foliation parallel stretching during $D_{2Ob}$, and are associated with a 25-50 m ankerite and siderite alteration halo.

In contrast, using a combination of high-resolution X-ray computed tomography and SEM, native gold, associated locally with extremely high grades, fills fractures in the quartz veins. These form high-grade ore shoots that are located in $F_{3Ob}$ fold hinges. Thus, mineralization hosted by thick, boudinaged quartz veins was controlled by later fracturing and folding of the quartz veins during $D_{3Ob}$. Chlorite porphyroblasts overprinting the $S_{3Ob}$ cleavage represent the proximal alteration of the quartz vein ores.

In summary, the results of this study indicate the Obuasi giant gold deposit formed mainly during two episodes of mineralization, marked by differences in style of mineralization and structural control. It is not yet known whether the two events are the products of two distinct hydrothermal events as has been interpreted in other giant deposits, e.g. Golden Mile, Boddington, or Ballarat (Bierlein et al., 1999; McCuaig et al., 2001; Bateman and Hagemann, 2004), or if the visible gold ore in the quartz veins is the product of gold remobilization from the disseminated ore.

9. Acknowledgments

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Chapter III:

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

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Chapter III: Arsenopyrite gold retention
1. **Abstract**

Quantitative electron backscatter diffraction analysis and ion microprobe imaging of gold-bearing arsenopyrites provide the first insights into the crystal plasticity and element mobility behaviour of highly enriched arsenopyrites through metamorphism (340° - 460° and 2 kbars). Remarkably, the arsenopyrites remained structurally and chemically robust during high strain deformation. It is only during a superimposed lower strain deformation event, at a high-angle to the preferred orientation of the arsenopyrites, that small amounts of crystal plasticity affected the arsenopyrites. During the low strain event a dissolution-reprecipitation reaction resulted in loss of gold from the crystal lattice, facilitated by localised domains of recrystallization, most likely due to fluid percolation along sub- and new grain boundaries. We suggest the abundance and robust nature of arsenopyrite in giant gold deposits affected by greenschist-amphibolite metamorphism is actually a critical factor in the preservation of those deposits.
2. **Introduction**

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

In contrast to arsenopyrite, the crystal plasticity of other sulphide phases such as pyrite, pyrrhotite, sphalerite, chalcopyrite, galena, stibnite and pentlandite have been investigated in detail (Barrie et al., 2011; Boyle et al., 1998; Cook et al., 1993; Cox, 1987; Kelly and Clark, 1975; McClay and Ellis, 1983; Vukmanovic et al., 2014). These studies conclude that crystal-plasticity of phases, such as pyrite, occurs relatively easily at temperatures as low as 260 °C and strain rates of approximately $10^{-12} - 10^{-16}$ s$^{-1}$ (Barrie et al., 2011) and can have a significant impact on trace element mobility (Reddy and Hough, 2013).

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

3. **Samples and methods**

In order to examine the crystal-plastic behaviour of arsenopyrite and its impact on trace element mobility, arsenopyrites with large enrichments of trace elements (Au, Ni) and well-constrained metamorphic-strain conditions were selected from the economic refractory ores of the giant Obuasi deposit. The mineralized arsenopyrites are hosted in paleoproterozoic sheared phyllites (2155 Ma, zircon U/Pb maximum age of deposition; Oberthür et al., 1998) composed of micas, quartz, carbonates (ankerite and siderite), chlorites, rutile and graphite. Arsenopyrite growth and mineralization occurred during continuous cleavage development and peak upper greenschist metamorphism at 340° - 460° and 2 kbars as shown by the development of strain shadows parallel with the continuous cleavage surrounding the arsenopyrites (the Eburnean orogeny: Schwartz et al. 1992; Oberthür et al. 1994; Fougerouse
et al. in press). Two representative grains from sample 215-20 are reported in this study, collected ~950 m below the surface from a 10 m wide high-strain domain associated with thick quartz veins, between two graphitic shear zones.

The arsenopyrites have been subject to two deformation events (Fougerouse et al., in press), mostly accommodating pure strain. The first event is high-strain, at the peak of metamorphism, which occurred during the Eburnean orogeny (D2ob; Fougerouse et al., in press). A pervasive, continuous cleavage developed while the quartz veins underwent boudinage, and strain shadows developed around the arsenopyrite grains (Fig. 1). The long-axes of the acicular arsenopyrites (up to 0.1x1 mm) are aligned parallel to the cleavage. A large minimum finite strain of 48% shortening and 235% stretch, perpendicular to the shortening, was estimated for the hosting phyllites from strain shadow length and fold periodicity (Fig. 1; p. 271 Ramsay and Huber, 1983), using oriented thin sections cut orthogonal to the cleavage and parallel to the lineation. Nonetheless, the arsenopyrite grains remain largely euhedral and relatively undeformed (Fig. 2). In the second event (D3ob), a low strain overprinting crenulation cleavage developed, representing a minimum shortening estimated at 15% with no associated stretch. The long-axes of the arsenopyrites are oriented at a high-angle to the later crenulation cleavage.

Backscattered Scanning Electron (BSE) imaging and Secondary Ion Mass Spectrometer (SIMS and NanoSIMS) investigations were carried out at the Centre for Microscopy, Characterisation and Analysis, University of Western Australia. BSE images were collected using a TESCAN VEGA3 SEM and ion imaging of $^{197}$Au were performed on a Cameca IMS 1280 ion probe on 150 x 150 μm areas. High-resolution elemental mapping was carried out using the Cameca NanoSIMS 50 with a spot size of approximately 100 nm. The experiment allowed detection of $^{197}$Au across areas measuring 100 x 100 μm with a 120 nm/pixel resolution. Quantitative maps of arsenopyrite crystallographic orientation were recorded using Electron Backscattered Diffraction (EBSD; Prior et al. 1999) at the CSIRO Australian Resources Research Centre in Kensington (Australia) using a Zeiss Ultraplus FEG SEM and at Curtin University using a TESCAN MIRA3 SEM. Systematic mis-indexing due to pseudosymmetry within the arsenopyrite grains was removed by identifying the axis and angle relationships to rotate the points and produce a correctly indexed grain.
Figure 1. A) Boudinaged mineralized quartz vein, Obuasi underground mine; B) Micrograph of mineralized metasedimentary ore, comprising gold-bearing arsenopyrites with quartz strain shadows deformed by a crenulation cleavage; C) Schematic of shear strain calculation estimation and equations used in D (modified after Ramsay and Hubert 1983); D) Frequency of shear strain ($e_{\text{stretch}}$) calculated from 100 strain shadows surrounding arsenopyrites.
4. Results

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

The EBSD data show a relative change in crystallographic orientation for each grain (Fig. 2 and 3). Consistent with other studies investigating sulphides crystal-plasticity (Reddy and Hough 2013) and silicate minerals (White, 1976), we define high-angle grain boundaries to have misorientations ≥10°. All boundaries <10° are classified as low-angle boundaries, representing subgrains. In most cases the intragrain variation does not reach 5°, though new grains are formed at a few localised points.

The analysis reveals a difference in the deformation intensity between grain 1 and 2 (Figs. 2 and 3). Grain 1 is parallel to the main cleavage (S2ob), in a domain unaffected by the later crenulation cleavage (S3ob), and contains only weak internal deformation (maximum of 3° misorientation). Conversely, grain 2 is located on a fold flexure of the S3ob crenulation. In this crystal, high densities of misorientations occur in a narrow localised domain, adjacent to a fracture (Fig. 3D). In this domain, the misorientations define low- and high-angle boundaries creating new small grains. In the centre top of the grain, an incipient domain of less than 3° misorientation is developed. The cumulative orientation profiles (Fig. 3H) along the short axis of grain 2 show minor misorientations (<2°), but much greater misorientations are achieved parallel with the long axis of the arsenopyrite (up to 7° from the tip of the grain to the core). Pole figure data indicates a dispersion of the orientation (Fig. 3). In addition, the pyrite crystal infilling the fracture of grain 2 is virtually undeformed (misorientation up to 2°; Fig. 3C).

The SIMS and NanoSIMS 197Au ion microprobe imaging reveals that the distribution of the gold is zoned within the crystals, with gold-rich A-rims around gold-poor cores (Fig. 2 and 3). The A-rims are in turn crosscut by gold-poor B-rims (Fig. 3F). The A-rims represent epitaxial zones with up to 1000 ppm Au (Fisher et al., 2014; Oberthür et al., 1994), although these concentrations decrease on the outer edges of the grain as shown on the left side of grain 2 (Fig. 3). An A-rim is well developed in grain 1 where minimal internal deformation
Figure 2. Sample 215-20, grain 1 - the arsenopyrite boundaries, cores and rims are highlighted in red. A) Backscattered electron (BSE) images; B) Cumulative orientation profile along line a-a’ (plotted relative to point a) parallel with the arsenopyrite long axis. Only minor crystallographic misorientations are recorded in the grain despite the wall rock being subject to high strain. C) Coloured EBSD maps showing crystallographic misorientations in the range 0-10°. Position of orientation profile a-a’ is indicated; D) SIMS elemental gold distribution map. The arsenopyrite is zoned with gold-poor core and gold-rich rim (A-rim).
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Figure 3. Sample 215-20, grain 2 - the arsenopyrite boundaries, cores and rims are highlighted in red; A-B) Backscattered electron (BSE) images; C-D) Coloured EBSD maps, showing crystallographic misorientations in the range 0-10° for C and 0-90° for D. Grain 2 coincides with a crenulation microfold and is weakly deformed by this later overprinting low strain event (D3ob), especially in zone D. High-angle boundaries (≥10°) are plotted in black and low-angle boundaries (≥2°) in red. Dynamic recrystallization has produced subgrains and new grains. Position of orientation profiles a-a’ and b-b’ are indicated; E-F) SIMS and NanoSIMS elemental gold distribution maps. B-rims are gold depleted in comparison to A-rims, and are well developed around zone F; G) Pole figures show the dispersion of orientation data; H) Cumulative orientation profiles (plotted relative to first point) parallel with the long axis (a-a’) and short axis (b-b’) of grain 2. The largest crystallographic misorientations are recorded along the crystal long axis (a-a’), parallel with the D3 shortening direction.
occurred. In grain 2, a large A-rim is cut by discontinuous B-rims, characterized by low Au signal. Internally, the A-rims are finely zoned with submicron-scale concentric bands with sharp boundaries (Fig. 3F; Fougerouse et al. accepted GCA). However, this fine epitaxial zoning in the domain of high misorientation identified in grain 2, appears blurry, with diffuse boundaries between bands and locally, small spherical high Au concentrations. The fuzzy gold signal in this domain is also dissected by numerous small scale, sharply defined B-rims with low Au signals. Critically, the overall B-rim width in this region of high densities of misorientations is up to three times greater in comparison with the domains of undeformed arsenopyrite.

5. Crystal-plastic evolution of arsenopyrites and consequences for gold Retention

The crystallographic misorientations and localised intragrain textures, revealed by EBSD, are consistent with dynamic recrystallisation by dislocation creep (Hirth and Tullis, 1992; Urai et al., 1986). In grain 2, this led to the development of subgrains and neoblasts accommodating crystal-plastic strain in a narrow localised domain, on the top right-hand side of the crystal. This crystal-plastic strain domain is coincident with a fracture filled with undeformed pyrite (Fig. 3). Overall, several significant features emerge from our analysis.

Firstly, grain 1 and grain 2 formed during high strain (D2 Ob, 50% flattening, >200% stretch) and upper greenschist metamorphism (John et al., 1999; Schwartz et al., 1992), then were subject to a second shortening event (D3 Ob, ~15% shortening), yet remained euhedral and underwent only minor crystal-plastic deformation. Secondly, grain 1 has minimal lattice distortion (≤3° of misorientation from grain tip to centre) in comparison to grain 2, which contains a localized domain of subgrains, neoblasts and microfracture. In this regard, grain 1 is located parallel to the S2 Ob cleavage, in a microlithon between two crenulation planes (S3 Ob), while grain 2 is located on a fold flexure of the S3 Ob cleavage. These relationships indicate that crystal plastic microstructures did not developed during the high strain peak metamorphic event, but during microfolding in the lower strain D3 Ob event, which only affected grain 2. Consistent with this interpretation, the orientation profiles (Fig. 3H) show that crystal-plasticity and the largest amount of lattice misorientation is recorded parallel to the D3 shortening direction. As the fold grew, the arsenopyrite initially underwent crystal-plastic deformation, then a fracture propagated through the arsenopyrite in the hinge, perhaps facilitated by embrittlement related to crystal-plastic strain hardening (Fleck et al., 1994). The fracture was infilled with undeformed pyrite (misorientation <2°), or alternatively, pyrite could have replaced the recrystallized arsenopyrite eased by stored stain energy. In either case, the minor amount of deformation in pyrite indicates that the arsenopyrite crystal-plasticity occurred early during D3 Ob microfolding.
We conclude that arsenopyrite is remarkably resilient to crystal plasticity between temperatures of 340° - 460° and pressures of 2 kbars. Arsenopyrites are acicular with a strong shape preferred orientation (SPO). Because there is a competency contrast between arsenopyrite and the quartz-phyllosilicate rich wall rock, at upper greenschist conditions, the SPO allows for accumulation of large strains in the wall rock, while grains aligned with the cleavage remain undeformed (Jessell et al., 2009).

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

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

The implications of our observations for trace element retention and loss in arsenopyrites are profound. Arsenopyrite is robust, maintaining its trace element content through conditions of high-strain and metamorphism of the wall rock. This behaviour is in contrast to other sulphides, such as pyrite, characterized by multiple slip systems that can be activated at temperatures as low as 260 °C (Barrie et al., 2011; Reddy and Hough, 2013). Such robust properties for arsenopyrite contribute to our understanding of its common association with world-class gold deposits. The ability of arsenopyrite to absorb gold into the crystal lattice and as nanoparticles (Cabri et al., 2000) establishes a clear link with mineralization. However, perhaps more importantly, its ability to maintain such trace element content through high strains means that precious metal resources are then preserved in the rock record. In this manner, arsenopyrite acts like an ark, encapsulating and preserving precious metals or trace elements. Furthermore, where crystal-plastic microstructures are developed, they are likely to enhance the release of precious metals such as gold from arsenopyrites undergoing reaction back to the natural environment.
Figure 2. Interpretation of the microstructural deformation sequence and replacement of arsenopyrite grain 2.
6. Acknowledgements

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Chapter IV:

Quantified, multi-scale X-ray fluorescence element mapping using the Maia detector array: application to mineral deposit studies

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Chapter IV: Synchrotron XFM mapping
1. **Abstract**

The Maia large solid-angle detector array and imaging system is capable of collecting high-resolution images of up to \( \sim 100 \) M pixels in size with dwell times of less than 0.2 ms per pixel and thus it is possible to document variation in textures associated with trace element chemistry by collecting quantified elemental maps of geological samples on the scale of entire thin sections in a short time frame (6–8 hr). The analysis is nondestructive and allows variation to be recognised on a centimetre scale while also recognising zonations at the micron scale.

Studies of ore systems require microanalysis of samples to collect information on mineral chemistry in order to understand physiochemical conditions during ore genesis and alteration. Such studies contribute to the debate on whether precious metals are remobilised or introduced in multiple hydrothermal events. In this study we demonstrate the microanalytical capabilities of the Maia large solid-angle detector array and imaging system on the X-ray fluorescence microscopy beamline at the Australian Synchrotron to provide data for these studies. We present a series of case studies from orogenic gold deposits that illustrate the power of the Maia detector for constraining chemical zonations in sulphides and associated alteration minerals, which can be used to decipher ore-forming processes associated with gold deposition. A series of large-area (<7 cm\(^2\)) elemental maps were collected with 2 to 4 \( \mu \)m pixel size using the Maia detector array. The data was processed using the GeoPIXE™ software package which allows variation in trace, minor and major element chemistry to be visualised in element maps. These maps are used to target further investigation with bulk spectra extracted and fitted for specific mineral grains and transects drawn through regions of interest. Analysis using the Maia detector offers a complementary method to map element distribution in geological samples that is both relatively fast and has a low detection limit for many elements of interest.
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2. Introduction

Studies of hydrothermal ore systems have traditionally included microanalysis of samples to collect information on mineral chemistry, mineralogy and texture (Cline, 2001; Cook et al., 2009b; Large et al., 2009; Sung et al., 2009; Cook et al., 2011; Large et al., 2013; Reich et al., 2013). Information from in situ microcharacterisation studies can be used to recognise both mineral zonations and chemical relationships among mineral phases that provide a record of hydrothermal activity, fluid chemistry and fluid-rock reactions. Such information is vital in constraining models of ore genesis. Microchemical data also informs metallurgical understanding and subsequent processing of characterised materials (Gregory et al., 2013).

Element mapping of geological materials utilises a range of techniques, with electron probe microanalysis (EPMA), scanning ion imaging using secondary ion mass spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) being most common. For all these techniques, there is a trade-off between spot size, or image resolution, the mappable area and the limits of detection for elements measured. LA-ICP-MS provides quantification for a wide range of trace elements with sub-ppm detection levels and can analyse relatively large areas; however, spot sizes are typically between 15 and 50 μm (Morey et al., 2008; Large et al., 2009; Large et al., 2013; Dare et al., 2014; Vukmanovic et al., 2014), and the technique is destructive to the sample surface.

Conversely, while EPMA is capable of a beam spot size of <1 μm, achieving low limits of detection requires high count times, limiting the area that can be mapped over a realistic time frame (Diehl et al., 2012; Reich et al., 2013). The scanning ion imaging method using SIMS has detection limits of 100–300 ppm for most elements, comparable to EPMA, and beam sizes of 2–15 μm are typical (Kusiak et al., 2013; Reich et al., 2013). Maps produced by scanning ion imaging typically have areas smaller than 1000 μm². Typically, individual mineral grains or small clusters of grains are analysed in studies of chemical zonations using these techniques. The technique is destructive to the sample surface.

The development of the Maia large solid-angle detector array and integrated real-time processor on the X-ray fluorescence microscopy (XFM) beamline at the Australian Synchrotron allows imaging of complex natural samples at high resolution (2-4 μm pixels) with images beyond 100 M pixels (Ryan et al., 2010a; Ryan et al., 2010b; Paterson et al., 2011). Detection limits of 10–100s of ppm are achievable at dwell times of <1 ms. Consequently, it is possible to document variation in textures associated with trace element chemistry by collecting whole thin section elemental maps in a short time frame (6–8 hr). The use of the Maia detector allows all phases in a thin section to be mapped at 2–4 μm resolution with detection limits comparable to, or exceeding, those achieved by EPMA for
most elements. The experimental conditions used provide quantified maps for elements with K-emissions (Ca to Zr) and L-emissions (Au, Pb, Hg, W, Bi, U) between 2.0 and 17.5 keV (Ryan et al., 2014). Maia uses full spectral data collection. Elements do not have to be selected prior to measurement because they are identified during peak fitting of the spectra during processing; this is an important distinction from other characterisation techniques such as EPMA and SIMS scanning ion imaging. Most importantly, XFM Maia analysis is nondestructive to the surface of the sample, allowing for follow-up analyses by other techniques such as electron backscatter diffraction (EBSD) or validation of key results against complimentary quantitative element mapping techniques, such as SIMS scanning ion imaging or LA-ICP-MS. Combining these techniques allows the study of high-grade gold deposition in relation to subtle proxies of the previous chemical and microstructural history of the host rocks.

One particular issue hotly debated within economic geology is the source of and deposition mechanisms for high-grade gold in orogenic gold systems (Groves, 1993; Large et al., 2009; Phillips and Powell, 2010; Tomkins, 2013). Analysis of pyrite and other sulphides has underpinned much of this debate. Understanding the distribution of Au and other elements within sulphides can help address many of the questions around ore formation and provide evidence for the timing of Au emplacement. We present three case studies from two orogenic gold deposits. Samples in two of the case studies are taken from the Sunrise Dam Gold Mine (SDGM). Gold at SDGM is contained within quartz-rich veins with little gold observed in the wall rock. Pyrite is the most common sulphide at the deposit and is present in variable amounts in ore zones and within alteration haloes in the country rocks (Yardley and Cleverley, 2013). The third case study sample is taken from the Obuasi gold mine. Gold mineralization at Obuasi is contained both in sulphides (mostly arsenopyrite disseminated in the metasedimentary host rock) and as visible gold in quartz veins (Oberthür et al., 1997; Yao and Robb, 2000).

These case studies illustrate the potential for Maia element mapping to address questions around Au emplacement and ore formation with data collected over a range of scales (μm to cm). The first and second examples examine the variation in sulphide phases around high-grade gold veins while the third considers the fine-scale alteration of sulphides. These case studies demonstrate the application of the Maia element mapping technique to solve problems relevant to economic geology.
3. X-ray fluorescence microscopy (XFM) mapping methods

X-ray fluorescence (XRF) microscopy was performed on the XFM beamline at the Australian Synchrotron (Paterson et al., 2011) using the Kirkpatrick-Baez mirror microprobe end-station. This provides a monochromatic 2 μm beamspot size for energies in the range 4–20 keV. Equipped with a Maia 384 detector array, the XFM beamline can acquire full spectral X-ray data for each detector at step sizes down to 2 μm over areas of several square centimetres (Kirkham et al., 2010; Ryan et al., 2010a) with count rates of ~4–10 M/s and energy resolution of 300–400 eV (recent upgrades to Maia 384C provide 240 eV resolution (Ryan et al., 2014)). Analysis of this spectral data, in real-time or in off-line processing, yields quantitative multi-element images with up to 100Mpixels. In case studies A and B, large-area (4–7 cm²) element maps were collected on each sample, with an incident beam energy of 18.5 keV, a pixel size of 4 μm and dwell times per pixel of 0.97 ms. The sample in case study C was mapped with a pixel size of 2 μm, dwell time of 7.8125 ms over an area of ~2 mm² to permit measurement of trace element concentrations with good counting statistics. Samples were prepared as polished petrographic thin sections of 30 μm thickness mounted on 1 mm-thick glass slides (case studies B and C) or as a 1 mm thick polished rock slab (case study A). The sample in case study C was mounted on a quartz glass slide to avoid the potential impact on As analysis from As present in some normal glass slides. Standard foils (Mn, Fe, Pt and YF₃) were analysed daily to allow calculation of the X-ray flux and monitor drift. X-ray penetration is not limited to a few microns, due to the high energy of the incident beam, so for each pixel, the concentration is an average of the whole volume sampled (Dyl et al., 2014; Ryan et al., 2014).

Maia uses full spectral data collection. Elements do not have to be selected prior to measurement because they are identified during peak fitting of the spectra during processing. The Maia XFM full spectral data were analysed using the GeoPIXE software suite which uses a fundamental parameters approach, with spectral deconvolution and imaging using the dynamic analysis method (Ryan, 2000; Ryan et al., 2010b), based on fitting a representative total spectrum and a detailed model of Maia detector array efficiency (Ryan et al., 2010a). Spectra are fitted using X-ray line relative intensities that reflect integration of yields and X-ray self-absorption effects for the given matrix or mineral phase and the contrasting efficiency characteristics across the detector array (Ryan et al., 2010a; Ryan et al., 2010b). The result is a matrix transformation that can be used in real-time or off-line projection of full spectral data into element maps. For the samples in this study, whole thin section maps
were initially produced by fitting the bulk spectra for the sample. Quantification of trace element concentrations within specific mineral phases was subsequently refined by extraction and refitting of spectra from the mineral phase of interest, with yields calculated using a specific matrix for that mineral.

4. Results

4.1. Case study A

The Maia element maps show multiple sulphide assemblages that are observed in the sample from Sunrise Dam, which represents the contact zone between potassic and sulphide altered wall rock and a gold-bearing quartz-carbonate vein. Sr, Ca, Fe and Mn maps show thin carbonate veins also cross-cut the wall rock, parallel or sub-parallel to the main vein contact, and these host coarse (1–2 mm) pyrite but contain no measurable gold.

The large-area maps (71×7 mm) of the sample show considerable variation in mineral chemistry moving into the gold-bearing vein (Fig. 1). A population of fine-grained (<200 μm) arsenian pyrite occurs within altered wall rock (Figs. 1 and 2). The coarser pyrite grains that sit within the thin carbonate veins have lower As content (As <0.1% in bulk pyrite grain analyses) than the wall rock population (0.1–0.25 % As in bulk pyrite grain analyses). The As content in the vein-hosted pyrite is more variable than that in the wall rock pyrite, with As-rich zones mainly formed around cracks in the pyrite grains (Figs. 1 and 2). The wall rock around the thin carbonate-bearing veinlets is bleached, devoid of the fine-grained sulphides within 2–3 mm of the veinlet. Pyrite grains in the gold-bearing quartz vein are coarse and show overgrowing As-enrichment zones, similar to those observed in the thin carbonate veins. Arsenic enrichment around fractures in the coarse pyrite is also observed. The abundance of Cu also varies across the sample. In the wall rock sulphides Cu concentration is low, while in the quartz-rich zones Cu is abundant and mainly associated with As, indicating the presence of tennantite. Tennantite occurs both as free grains within the quartz vein and as inclusions within pyrite grains. Coarse gold grains are hosted by quartz within the vein, and finer-grained gold is present as inclusions within pyrite in the quartz vein and the pyrite veinlets (Fig. 2). Trace element variations are also observed in the non-sulphide rock matrix. Figure 2d shows variation in Sr, Rb and Zr across the wall rock-vein contact. Over a 19.9 mm transect (x-x’) across the contact, the strontium content varies from below detection limit (<10 ppm) to almost 1000 ppm (Fig. 2e). Detection limits depend on counting statistics and, for XFM imaging, scale generally with the inverse square root of the dwell time per point. In the case of this transect, each data point corresponds to a total dwell time of 32 ms over an area of 8×64 μm².
Fig. 1 a A slab from Sunrise Dam (case study A—sample GQ1943_3) with the white box indicating the area mapped by Maia detector. The dashed white lines indicate veinlet margins and the dashed black line indicates the main wallrock-vein contact. b Large-area element maps of the sample show heterogeneity in the distribution of elements from wall rock into veins. Individual element maps are presented for Fe, Rb, Sr and Zr. Black zones indicate that element was not detected; blue, low concentrations; yellow, high concentrations. Two RGB composite maps are presented. The subareas shown in Fig. 2 are indicated by white boxes. Full-resolution versions of the maps presented in this figure are available through the CSIRO online data repository (Fisher and Ryan 2014)
Fig. 2 Selected subareas highlight variation in mineral chemistry and zonation patterns in sulphides across the Sunrise Dam sample in case study A. a, b and c Three different sulphide populations are shown in RGB maps. d Trace element variations across the wall rock-vein contact are shown in an RGB map of Rb, Sr and Zr. e A transect (x-x’) shows the quantified variation in Sr across the contact and parallel carbonate veinlets. The detection limit for Sr is 10 ppm for a total dwell time of 32 ms per transect point.
4.2. Case study B

Elemental maps processed from the bulk spectral data from the sample from Sunrise Dam show sulphide bands in a foliated wall rock truncated by a carbonate vein (Fig. 3a). The full section maps of Fe, As and Ca distribution indicate variation in the distribution of As within these sulphide bands across the length scale of the section. On the left side of the carbonate vein, the bands contain extensive, fine-grained (5–150 μm) As-dominant minerals as well as showing As zonation and inclusions within coarser (50–350 μm) pyrite grains (Fig. 3b). On the right side of the vein, the As minerals are much less abundant (Fig. 3c). Arsenic zonation within pyrites appears similar to that within the coarser pyrite on the left side of the vein. Some pyrite grains on the right side of the vein show atoll structures with As-rich cores (Fig. 3c). Fine-grained Au (<5–12 μm) forms inclusions within the pyrite grains on both sides of the vein. When bulk chemical compositions are extracted for 20 pyrite grains on each side of the carbonate vein, a comparison of As and Cu concentrations in each population shows that Cu concentrations in the pyrite grains on each side of the vein are comparable, between 2000 to 4000 ppm in all grains analysed. Conversely, the As concentrations in pyrite grains on the left reach a maximum of 8.9 wt%, more than double the maximum in pyrite grains on the right side of the vein (Fig. 3d).

Spectra for an arsenian, Au-bearing pyrite (Fig. 4) were extracted and refitted to optimise the quantification (Fig. 4c). Chemical data along a transect (y-y') through a selected pyrite grain show the variation in As, Cu and Au at 4-μm spacing (Fig. 4). The concentration of arsenic within grain A (Fig. 4) ranges from 0.1 to 6 wt%. Variations in Cu and Zn concentrations in the analysed pyrite grains ranged from <0.1 to 2.5 wt% and <0.04 to 0.75 wt%, respectively. For most features within a 30 μm-thick thin section, it is appropriate to assume a constant composition for the entire thickness of the section. However, for discrete phases with diameters less than the thickness of the section, this does not apply, such as for small gold grains within sulphides. When a subregion containing Au (largest yellow grain—Fig. 4b) is analysed, initially assuming uniform concentration with depth, a concentration of ~22 wt% Au is measured. This indicates that the full thickness of the thin-section in that pixel is not composed entirely of Au; this therefore indicates either a thin grain of Au at the surface or that Au is present as a discrete, buried phase within the thin section. Petrographic analysis confirms Au is not at the surface of the section, and consequently, the Maia mapping has located a buried phase.
Fig. 3 Maps of the Sunrise Dam sample (WSZ-A) in case study B. a Whole thin section element maps of As, Fe and Ca are combined to produce an RGB image (As, red; Fe, green; Ca, blue) of a carbonate vein crosscutting a foliated wall rock with sulphide banding. Examination of elemental distribution indicates b higher As content in the sulphide band in the wall rock on the left of the carbonate vein and c lower As content in the sulphide band in the wall rock on the right of the carbonate vein. The white box indicates the area shown in Fig. 4. d Cu vs. As plot for pyrite from the left (black square) and right (open circle) sides of the carbonate vein in case study B. Pyrite on the right side shows a relatively constant Cu to As ratio whereas pyrite on left side is relatively enriched in As
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Fig. 4  a An RGB image (Ca, red; Fe, green; As, blue) of a subregion containing pyrite grains with As zonation and Au inclusions. b Au (yellow) and Cu (blue) distribution in the same region shown in a. c Spectra extracted for a pyrite grain show the presence of the Au (Lα) peak on the shoulder of the As (Kα) peak. d Transect y-y’ through the pyrite grain shows variation in As, Cu and Au concentrations. Detection limits for the elements shown are 278 ppm for Fe, 214 ppm for As and 279 ppm for Au with a total dwell time of 44 ms per transect point.
4.3. **Case study C**

Example C is taken from the Obuasi gold mine, and the element map represents an aggregate of euhedral to partially-fragmented arsenopyrite crystals within a mica schist (Fig. 5). Gold mineralization at Obuasi is contained both in sulphides (mostly arsenopyrite disseminated in the metasedimentary host rock) and as visible gold in quartz veins (Allibone et al., 2002b). In example C, the distribution of major elements Ca, Fe and As (Fig. 5a) reveals a matrix composed of ankerite, muscovite, chlorite and quartz, whereas the sulphide mineralogy is arsenopyrite with minor pyrite. Figure 5b displays selected trace elements (Au and Ni) concentrated in the sulphides. On the spectra (Fig. 5c), the gold peaks are distinguished in the signal from the arsenopyrite despite the peak overlap and high concentration of arsenic in the sample.

The gold concentration in arsenopyrite ranges from <1000 up to 4000 ppm, contained within multiple, narrow bands that appear to be crystallographically controlled around consistently gold-poor cores (Fig. 5b, d). The arsenopyrite cores are also slightly enriched in Ni. The gold zonation associated with epitaxial overgrowth was previously described using SIMS scanning ion imaging (Oberthür et al., 1997). In addition to the crystallographically controlled gold, gold grains are found in healed microfractures in the arsenopyrite and pyrite and rarely as inclusions in the arsenopyrite. Nickel concentrations vary in pyrite, defining nickel-rich cores and nickel-poor rims. Nickel also substitutes into narrow rims on limited sections of some arsenopyrite (Fig. 5b).

Along healed microfractures and grain boundaries (Fig. 5), the major and trace element concentrations vary from the bulk mineralogy. Transect z-z' (Fig. 5d) follows the same primary overgrowth rim (Fig. 5b), demonstrating that arsenic, iron, nickel and gold concentrations vary close to a microfracture at ‘z’, which has been infilled with secondary arsenopyrite. Arsenic and nickel concentrations are higher close to the microfracture (z) whereas the iron and gold concentrations are lower in the same zone. Gold concentrations decrease by approximately 30 %, whereas nickel concentrations change from below the detection limit (75 ppm per transect point) in the rim to up to 4000 ppm close to the fracture.
**Fig. 5** XFM elemental maps of Obuasi sample 215-7b. 

- **a** An RGB image (Red, calcium; green, iron; blue, arsenic) of a sulphide aggregate. The sulphides are pyrites and gold-bearing arsenopyrites. The gold concentration is zoned with higher concentration in epitaxial overgrowth whereas the cores are gold-poor. Nickel is enriched in pyrite cores and along microfractures and grain boundaries in arsenopyrites. The positions of transect z-z’ are indicated.

- **b** Yellow, gold; blue, nickel distribution in the same region shown in **a**. As, Fe, Ni and Au concentrations along transect z-z’, the decreases in As and Fe at 70 and 250 mm are due to late brittle fractures. Gold concentration decreases by 30 % adjacent to a microfracture cemented with a secondary arsenopyrite, whereas the nickel concentration is high in the same zone due to pseudomorphic replacement of the primary arsenopyrite.
5. Discussion

Analysis of samples using the Maia detector and synchrotron radiation is a technique for mapping the distribution of elements of interest in geological samples. It is an effective method for determining the concentrations and distribution of several elements that occur at low-level concentrations. The technique has a broad application in the study of geological materials, both for large-area mapping (e.g. Dyl et al. 2014 mapping of meteorite samples) and locating and mapping the distribution of rare phases such as Au or PGEs (Lintern et al., 2013; Ryan et al., 2013) in geological and biological matrices. Other potential applications include imaging subtle trace element zonations in silicate and carbonate minerals and examination of trace element mobility associated with grain boundaries and microstructures.

Arsenic and antimony are common contaminants in gold and copper processing streams. Similarly, much of the refractory gold in mineral deposits is thought to be ‘invisible’ gold, either nanoparticulate gold or in gold in solid solution within sulphides (Large et al., 2009; Sung et al., 2009; MacKenzie et al., 2014). The knowledge of the distribution of both the value and deleterious elements in ore material is extremely important for evaluating the value of ore and assessing whether these elements also can be extracted or concentrated during mineral processing, feeding into mine and mill planning.

Recognition of trace element variation is also critical for understanding processes of ore formation and hydrothermal alteration. Variations in trace element chemistry and zonation in minerals can record changes in physicochemical conditions during mineral growth. These variations can be fully recognised through high-resolution, whole-section mapping using XFM and the Maia detector. The case studies presented in this contribution demonstrate the application of this method to sulphide chemistry; this technique is, however, applicable to many mineral phases. In case studies A and B, variations in As and Cu content coupled with textural and grain size observations allow multiple populations of pyrite to be discriminated, which can be used to interpret the fluid-rock reaction history with implications for genetic models. Initial wall rock alteration in the sample in case study A is characterised by a potassic overprint with extensive As-rich fine-grained pyrite. Cross-cutting veins are associated with the dissolution of pyrite, with fine-grained pyrite absent around veinlets and precipitation of coarse-grained pyrite with lower bulk As content within the veinlets. The pyrite is subsequently overgrown and overprinted with further enrichment of As in overgrowth zones and along fractures in the coarse-grained pyrite. The veining event associated with coarse gold emplacement seen in case study A is also associated with Cu, forming sulphosalts. Inclusions of Au and sulphosalts within the latter, coarse pyrites indicate that this population of pyrite formed contemporaneously with Au emplacement.
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Arsenic is an effective pathfinder for Au in many orogenic gold systems. However, the textural observations of As, Cu and Au distribution in pyrite in this study indicate that there were multiple fluid events that mobilised these elements to different degrees. The variation in As in the pyrite grains on either side of the carbonate vein in case study B indicates that As-rich fluids flowed along permeable horizons within the foliated wall rock. Whereas coarse gold is mainly localised within veins, the presence of fine-grained Au inclusions in As-rich pyrite in the wall rock indicates that the As-rich fluids may also have been Au bearing.

The variation in major and trace elements associated with microfracture and grain boundaries in case study C is interpreted as indicating that gold concentration has been modified from the primary zoning of the grains by pseudomorphic replacement (Harlov et al., 2005; Putnis, 2009). Oberthür et al. (1997) previously described gold distribution in arsenopyrite at Obuasi using SIMS scanning ion imaging, attributing the highest concentrations of gold to the epitaxial overgrowth of the arsenopyrite grains. However, the studies were restricted by the limitations of the scanning ion imaging technique at that time to a 30 μm spot size and a map area of 120 μm in diameter. In contrast, individual arsenopyrite grains at Obuasi are often up to 1 mm across, and full characterisation of the gold textures in the grains requires resolution at the micrometre scale. The high spatial resolution (2 μm spot size) and multi-element analytical capability that XFM Maia analysis provides are tools to understand complex mineral and alteration relationships over large sample areas of several square centimetres. Data collected can be binned over a range of length scales allowing for chemical quantification of both micro- and macro-features. An advantage of Maia XFM analysis is the ability to detect micrometre-scale grains at any depth within sections of 10s of microns in thickness with an image with spatial resolution determined by the beam spot size (Ryan et al., 2013). This permits distinction between Au inclusions within pyrite and dispersed Au in the matrix of the sulphide and even the determination of particle depth.

6. Summary and conclusions

The Maia detector on the XFM beamline at the Australian Synchrotron allows collection of high-resolution elemental maps over whole thin sections with detection limits for many trace elements that are comparable with, or better than, EPMA. The step change in mappable area and resolution of this method, compared with EPMA, LA-ICP-MS or SIMS scanning ion imaging analysis, offers the opportunity to fully recognise and quantify variation in
mineral chemistry in a sample from whole section length scales to micron scales and to not miss rare precious metal phases located at depth within a sample section.

Maia uses full spectral data collection. Elements do not have to be selected prior to measurement because they are identified during peak fitting of the spectra during processing; this is an important distinction from other characterisation techniques such as EPMA and SIMS scanning ion imaging. Most importantly, Maia XFM analysis is non-destructive allowing for follow-up analyses using other techniques such as electron backscatter diffraction (EBSD) or validation of key results against other quantitative element mapping techniques such as SIMS or LA-ICP-MS.

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8. References

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Chapter V:

Gold remobilisation and formation of high grade ore shoots driven by dissolution-reprecipitation replacement and Ni substitution into auriferous arsenopyrite

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1. Abstract

Both gold-rich sulphides and ultra-high grade native gold oreshoots are common but poorly understood phenomenon in orogenic-type mineral systems, partly because fluids in these systems are considered to have relatively low gold solubilities and are unlikely to generate high gold concentrations. The world-class Obuasi gold deposit, Ghana, has gold-rich arsenopyrite spatially associated with folded quartz veins, which contain extremely high concentrations of native gold overprinting the microcrack networks within the fold hinges of the quartz veins. Here, we examine selected samples from Obuasi using a novel combination of quantitative electron backscatter diffraction analysis, ion microprobe imaging, synchrotron XFM mapping and geochemical modelling to investigate the origin of the unusually high gold concentrations. The auriferous arsenopyrites are shown to have undergone partial replacement (~15%) by Au-poor, nickeliferous arsenopyrite, during localised crystal-plastic deformation, intragranular microfracture and metamorphism (340°-460°C, 2 kbars). Our results show the dominant replacement mechanism was pseudomorphic dissolution-reprecipitation, driven by small volumes of an infiltrating fluid that had relatively low $f_{S_2}$ and carried aqueous NiCl$_2$. We find that arsenopyrite replacement produced strong chemical gradients at crystal-fluid interfaces due to an increase in $f_{S_2}$ during reaction, which enabled efficient removal of gold to the fluid phase and development of anomalously gold-rich fluid (potentially 10 ppm or more depending on sulphur concentration). This process was facilitated by precipitation of ankerite, which removed CO$_2$ from the fluid, increasing the relative proportion of sulphur for gold complexation and inhibited additional quartz precipitation. Gold re-precipitation occurred over distances of 10 μm to >50 m and was likely a result of sulphur activity reduction through precipitation of pyrite and other sulphides. We suggest this late remobilisation process may be relatively common in orogenic belts containing abundant mafic/ultramafic rocks, which act as a source of Ni and Co scavenged by chloride-bearing fluids. Both the preference of the arsenopyrite crystal structure for Ni and Co, rather than gold, and the release of sulphur during reaction, can drive gold remobilisation in many deposits across broad regions.
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2. Introduction

Trace element remobilisation occurs when an element contained in a primary mineral is released from the crystal structure, allowing it to be transported to new locations, often at high concentrations, a short distance away (millimetres to hundreds of metres; Marshall et al. 2000). This type of remobilisation is particularly relevant to understanding the distribution of precious metals in deformed and metamorphosed ore deposits. But our understanding of how trace elements are remobilised is also critical to a wide range of environments, including gold transport in the regolith profile of weathered terrains (Hough et al., 2007), mobility of deleterious metals in soils (Chuan et al., 1996; Kalbitz and Wennrich, 1998) and potentially disturbed geochronological isotope systems in zircons and monazites (Geisler et al., 2007; Harlov et al., 2011; Reddy et al., 2006). However, when it comes to precious metal remobilisation under mid-crustal conditions the process is controversial due to the inferred low solubilities of these elements in aqueous fluids, the extremely slow rates of element diffusion in minerals and poor understanding of how metals are soluble in one location but re-precipitated just a short distance away. Despite these arguments, there is a common spatial relationship between primary sulphides containing trace metals in their crystal structure, and nearby, texturally younger concentrations of those metals, often at very high grades (Cook et al., 2009; Cook et al., 2013; Dubé et al., 2004; Fougerouse et al., in press; Large et al., 2007; Morey et al., 2008).

Metal migration has been documented in volcanic massive sulphides (VMS) systems (Cook et al., 1998; Cook, 1996; Le Vaillant et al., 2015; Marshall and Gilligan, 1993; Tomkins, 2007), iron ore systems (Angerer et al., 2013; Duuring and Hagemann, 2013) and also in gold systems (Cook et al., 2009; Cook et al., 2013; Dubé et al., 2004; Morey et al., 2008; Tomkins and Mavrogenes, 2002; Tomkins et al., 2004). Although some of the mechanisms involved in this remobilisation are not understood, remobilisation led to the migration of Ni up to 250 m away from the primary mineralisation of the Mitel Ni sulphide deposit (Le Vaillant et al., 2015), the significant upgrade of hypogene ores at the Beebyn iron deposit (Duuring and Hagemann, 2013) and spectacular native gold occurrences in the Red Lake gold deposit (Dubé et al., 2004).

In this study, we investigate the well-documented Obuasi gold deposit, Ghana (Allibone et al., 2002; Fougerouse et al., in press; Oberthür et al., 1994), which provides a natural laboratory to address the issue of remobilisation, due to the presence of very high concentrations of native gold in the hinges of folded quartz veins and a spatial association with gold-rich arsenopyrite in metasedimentary wall rocks. Our previous work has demonstrated that arsenopyrite crystals in the wall rocks have lost some of their gold content.
during deformation (Fougerouse et al., submitted). In this study, we combine state-of-the-art analytical methods (X-ray fluorescence synchrotron mapping, high resolution secondary ion mass spectrometry, electron backscattered diffraction and scanning electron microscopy) to examine the distribution of gold across multiple scales and identify the mechanisms that may have contributed to the loss of gold from arsenopyrite and its reprecipitation in native form.

3. Previous studies on trace element remobilisation

At the mineral scale, three mechanisms are linked to trace element mobility; (1) fluid-mediated replacement; (2) intragrain diffusion and; (3) partial melting of the sulphide ore. The partial melting of sulphide ores has been interpreted to occur in high-grade metamorphic mineral deposits (Bailie and Reid, 2005; Frost et al., 2002; Mavrogenes et al., 2001; Sparks and Mavrogenes, 2005; Tomkins et al., 2007; Tomkins et al., 2004), but also at greenschist facies conditions and temperatures as low as 400 °C (Biagioni et al., 2013; Ciobanu et al., 2006). This process is possible due to the presence of low-melting-point chalcophile elements (LMCE), which significantly lower the melting temperature of the sulphides. These low temperature melts have the capability to scavenge metals with high melting points such as gold (Ciobanu et al., 2006; Tooth et al., 2008; Tooth et al., 2011), potentially allowing a zone refining process to persist long after formation of the primary deposit (Cockerton and Tomkins, 2012). The melt usually crystallises as multi-mineral clusters of sulfosalts, tellurides, sulphides and native metals, with curviplanar boundaries and droplet-shaped minerals (e.g., Voudouris et al. 2013). In the system Fe–As–S, the first melt can appear at temperatures as low as 281°C (Frost et al., 2002), but only at S fugacity (fS) conditions above the stability of arsenopyrite (see Tomkins et al., 2004).

Intragrain diffusion is potentially important in various minerals for trace element remobilisation and operates via a broad range of sub-mechanisms, the three most important being volume diffusion, high diffusivity pathway diffusion and dislocation–impurity pair (DIP) diffusion (Klinger and Rabkin, 1999; Plümper et al., 2012; Reddy et al., 2007; Timms et al., 2011; Vukmanovic et al., 2014). In the diffusion model, the migration of large atomic radii elements such as gold is best explained by high diffusivity pathway and DIP diffusion sub-mechanisms (Plümper et al., 2012; Reddy et al., 2006; Vukmanovic et al., 2014), whereas the volume diffusion mechanism is usually regarded as being too slow to be effective at mid-crustal temperatures (~300-450 °C). As a result of the migration of dislocations and elements in minerals, primary internal crystallographic zoning is usually at least partially erased and becomes diffuse or non-existent, whereas major element compositions remain unchanged. The operation of these diffusion mechanisms have been interpreted to explain rare earth element redistribution in zircons (Reddy et al., 2006; Valley
et al., 2014) and trace element compositional variation and phase exsolution in sulphides hosted in mineral deposits (Reddy and Hough, 2013; Tomkins and Mavrogenes, 2001; Vukmanovic et al., 2014).

Fluid-mediated replacement reactions, or coupled dissolution-reprecipitation reactions (Putnis, 2009), are potentially an extremely effective mechanism for major and trace element modifications in minerals (Geisler et al., 2007; Harlov et al., 2011; Xia et al., 2009; Zhao et al., 2009). This reaction occurs when elements introduced by a fluid cause a mineral phase to be replaced either by a new composition of the same phase or by an entirely new phase (Harlov et al., 2011). In the case of one phase being replaced by a new composition of the same phase, the solid solution composition (i.e. non-stoichiometric) of the parent phase has higher solubility in the fluid than the pure stoichiometric end-member of the daughter phase (Geisler et al., 2007; Lippmann, 1980). Trace elements within the parent phase can be stripped out during the reaction and released into the fluid (Martin et al., 2008). Once initiated, the reaction is self-perpetuating (Harlov et al., 2011). The reaction front is sharp, planar to curvilinear and associated with a thin layer of supersaturated fluid film during reaction. The daughter phase can be characterised by interconnected nano- and micro-porosity allowing fluid infiltration to and from the reaction front (Putnis, 2009). In some examples, at advanced stages of the reaction, the interconnected nano- and micro-porosity is not preserved due to complete recrystallisation of the daughter phase and sealing of the porosity (Harlov et al., 2011). In systems similar to what is under discussion here, gold micronuggets have been observed where arsenopyrite replaces löllingite, particularly along replacement reaction fronts (Neumayr et al., 1993; Tomkins and Mavrogenes, 2001).

4. Sample suite and microanalytical methods

4.1. Sample suite

A representative set of samples were selected from the Obuasi gold deposit (Ghana). Obuasi is the largest gold deposit discovered in West Africa with about 62 Moz of gold (past production + resources). The host rocks and geological context of the Obuasi deposit are well-documented (Allibone et al., 2002; Fougerouse et al., in press; Oberthür et al., 1994; Yao and Robb, 2000) and shown in Figure 1. The deposit is hosted in the Paleoproterozoic Birimian Kumasi volcanosedimentary basin composed of carbonaceous phyllites, slates, psammites, and volcano-sedimentary rocks (Adadey et al., 2009; Oberthür et al., 1998; Perrouty et al., 2012). The metamorphic conditions were calculated from the mineral assemblage actinolite + chlorite + clinzoisite + quartz + calcite, to have been 340° - 460° and 2 kbar (Schwartz et al., 1992). Samples were collected from the underground
mineralised exposures of the Obuasi mine (drives L30#1-XC318; L30#2-XC215; L21-XC343; L29-XC317; L35-XC283). The main host for the sulphide ores are phyllites composed of micas, quartz, carbonates (ankerite and siderite), chlorites, rutile and graphite.

Two economic styles of mineralisation coexist in the same ore zone; gold-bearing arsenopyrite disseminated in the metasedimentary rocks and native gold in dense fracture networks developed in the hinges of folded quartz veins (Blenkinsop et al., 1994; Fougerouse et al., in press; Oberthür et al., 1994). Arsenopyrite is the dominant ore mineral (60-95%) but pyrite can also be present (Oberthür et al., 1994). Concentrations of gold in the crystal lattice of the arsenopyrites range from 300 to 3000 ppm (Fisher et al., 2014; Fougerouse et al., in press), whereas gold content only reach up to 3.3 ppm in pyrite (Oberthür et al., 1994). Although the two styles of mineralisation are spatially associated with one another, they formed during distinct structural events (Fougerouse et al., in press), with gold-bearing arsenopyrite crystallising during early D2Ob whereas the native gold precipitated during D3Ob.

Evidence for the timing of arsenopyrite mineralisation includes (Fougerouse et al., in press) quartz-ankerite strain shadows around the arsenopyrites that are parallel with a pervasive S2Ob fabric but refolded by a S3Ob crenulation cleavage. Evidence for the timing of native gold mineralisation in adjacent quartz veins includes (Fougerouse et al., in press) the distribution of the gold in fracture networks in F3Ob fold hinges of the quartz veins, which are semiparallel with the S3Ob crenulation cleavage. Notwithstanding these observations, both styles of mineralisation likely formed within a short time of one another during the Eburnean orogeny, which affected the West African Craton from 2125 to 1980 Ma (Perrouty et al., 2012).

4.2. Analytical methods

We used a diverse combination of microanalytical techniques to investigate the elemental distribution of trace elements (particularly Au) in the gold-bearing arsenopyrites and their relationship with microstructures formed during crystal-plasticity.

X-ray fluorescence (XRF) mapping provided quantitative multi-element images with their full petrographic context. The application of the method to ore mineral studies is well documented in Fisher et al. (2014). The analyses were performed on the XFM beamline at the Australian Synchrotron (Paterson et al., 2011) using the Maia 384 large angle detector array (Fisher et al., 2014; Kirkham et al., 2010; Ryan et al., 2010a; Ryan et al., 2014). The samples were mapped with a pixel size of 2 μm and dwell time of 7.8125 ms, over areas of a few square millimetres, to permit measurement of trace element concentrations with good
counting statistics. Samples were prepared as polished thin sections (30 μm thick) mounted on 1 mm-thick quartz glass slides to minimise arsenic background from the glass slide (Fisher et al., 2014). Standard foils (Mn, Fe, Pt and YF3) were analysed daily to calculate the X-ray flux and monitor drift. The Maia XFM full spectral data were analysed using the GeoPIXE software suite. GeoPIXE applies a fundamental parameters approach, with spectral deconvolution and imaging, using the dynamic analysis method (Ryan, 2000; Ryan et al., 2010b) based on fitting a representative total spectrum and a detailed model of Maia detector array efficiency (Ryan et al., 2010a). The Maia detector has a resolution of 400 eV which allows gold peaks to be distinguished in the spectra despite the peak overlap with arsenic (Fisher et al., 2014).

Elemental mapping was carried out using the Cameca NanoSIMS 50 at the Centre for Microscopy, Characterisation and Analysis (CMCA) at The University of Western Australia. The samples were prepared as polished one inch resin mounts and thin sections, and carbon coated to provide conductivity. Measurements were performed with a Cs⁺ primary beam, with a spot size of approximately 100 nm, impact energy of 16 keV, and a beam current of 2 pA. The instrument was operated in multicollector mode, allowing the simultaneous detection of five ion species (34S, 54Fe32S, 60Ni32S, 75As32S and 197Au) from the same analysis region. Secondary ion images were obtained by rastering the primary ion beam across areas measuring 100 x 100 μm, at a resolution of 1024 x 1024 pixels (each pixel measuring approximately 97 nm), with dwell times of 21-40 ms per pixel. Prior to imaging, the sample surface was presputtered with the primary ion beam (using 250 pA beam current) to > 2 x 10¹⁷ ions/cm², in order to remove surface contamination and implant Cs⁺ ions to reach a steady-state of ion emission.

Mineral identification, mineral chemistry zonation, overprinting relationships and paragenesis were investigated with optical techniques and scanning electron microscopy (SEM). Backscattered electron images were generated using a TESCAN VEGA3 SEM. Energy Dispersive X-ray spectra (EDX) were acquired using an Oxford instruments X-Max 50 silicon drift detector with AZtec software fitted on the TESCAN VEGA3. Analytical conditions were 15 kV accelerating voltage with a 1.5 nA probe current.

Electron backscatter diffraction (EBSD) and EDS data were collected on 1 inch round polished block at the CSIRO Australian Resources Research Centre in Kensington (Australia) using a Bruker e-flash detector for EBSD and a Bruker XFlash 5030 silicon drift detector for EDS, all fitted on a Zeiss Ultraplus FEG SEM. The instrument was operated at 20 kV accelerating voltage, 12.10 nA beam current and a tilting angle of 70°. EBSD colours maps show the minimum crystallographic misorientation from a reference point at the centre of each grain.
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Fig. 1. (A) Geology of northern Ghana Paleoproterozoic basement (simplified from Allibone et al., 2002). The Obuasi giant deposit is located in the Kumasi Group metasedimentary rocks close to the contact with the Sefwi Group volcanic greenstones of the Ashanti belt. (B) Typical mineralised and laminated quartz vein, containing wall rock fragments, from Obuasi underground drive, level 30#1 Crosscut 318; (C) Microphotograph of the sediment sample DF038 (phyllites). Gold-bearing arsenopyrites are surrounded by quartz strain shadows parallel with S_{2_{Ob}} and refolded by S_{3_{Ob}}; (D) BSE image of mineralised quartz vein sample DF091b, native gold precipitated along muscovite cleavage planes and developed in fractures crosscutting the quartz veins. The dominant fracture is parallel with the hinge line of S_{3_{Ob}} crenulation cleavage; (E) Textures in gold-bearing arsenopyrites (BSE sample 318-15). The arsenopyrite grains are euhedral and native gold is present in microfractures and grain boundary regions. Apy_{II} has a higher atomic mass; (F) Fracture in quartz vein filled with gold and accessory sulfides (sample DF099 - BSE image).
5. Descriptive properties of arsenopyrites, mineral assemblages and native gold distribution

Maia XRF maps, of sample 215-7b are presented in Figures 3 and 5. The matrix is composed of quartz, muscovite, chlorite, ankerite and siderite. The sulphides form aggregates of partially-fragmented arsenopyrite grains and small pyrites. High resolution NanoSIMS elemental maps of areas up to 100 x 100 μm² allowed investigation of the fine textures of the trace element distribution and the contact between the different domains of the arsenopyrites and microfractures (Figs. 3, 4 and 6).

5.1. Arsenopyrite overgrowths and rims

Mineralised arsenopyrites are generally idiomorphic, acicular and range from 50 μm up to several mm in size. Gold-bearing arsenopyrite is the major component of the disseminated sulphide ores (60-95% - Fig. 1) with lesser pyrite, pyrrhotite, marcasite, and chalcopyrite. The sulphide mineralisation is surrounded by a 50 m wide ankerite and siderite alteration halo and the arsenopyrites are commonly surrounded by quartz-ankerite strain shadows developed during D2Ob (Fougerouse et al., in press). The smaller grains are usually homogenous (inclusion-free) under optical microscope, whereas the bigger grains are typically composed of several domains detailed below. The arsenopyrite also contains microfractures and interstitial spaces between grains, filled with ankerite, pyrite and small gold particles, which are interpreted to form during D3Ob (as discussed in section 6).

5.2. Crystallographically controlled microtextures and chemistry

The arsenopyrite grains are composed of at least two primary domains: rims that appear homogenous in BSE images and inclusion-rich cores (Oberthür et al., 1994; Oberthür et al., 1997). The cores contain inclusions of pyrrhotite, chalcopyrite and rutile. The boundary between cores and rims can be rich in silicate inclusions (Figs. 1 and 2). In this study, the combination of the core-and-rim domains are abbreviated as Apy(I). The composition of Apy(I) is non-stoichiometric, being depleted in As (~44 wt% As – table 1). The distribution of the gold in Apy(I) is zoned (Fig. 3), with gold-poor cores and gold-rich rims (300 to 3000 ppm Au in the rims; Fougerouse et al. in press; Fisher et al. 2014).

In the Apy(I) rims high-resolution NanoSIMS mapping reveals that Au is distributed in alternating, sub-micrometer-scale concentric bands (up to 100) with sharp boundaries, despite the homogenous appearance of the Apy(I) in BSE imagery. Gold is the only
compositional variation between the bands and none of the other major or trace element chemistry changes were observed. The bands are concentric and parallel with the euhedral morphology of the grain boundary of the arsenopyrite (Figs. 3, 4 and 6). Each band is typically less than one micrometer wide, with variable gold content relative to one another and a semi-regular spacing. No micronuggets of native gold were detected in the arsenopyrite grains at the highest resolution of our analysis (100 nm), except in association with microfractures.

Commonly, a third arsenopyrite domain cuts across the mineralised grains, penetrating in from microfractures and grain boundaries. These domains, labelled ApY(II), are characterised by higher As and lower S concentrations, with compositions that are close to stochiometric (~46 wt% As – table 1). ApY(II) domains are nickeliferous and gold-poor. Critically, these gold-poor domains preserve the original shape of the arsenopyrite grains and the contacts between ApY(II) and ApY(I) are sharp, ranging, in the same grains, from planar to curved (Fig. 2). NanoSIMS imaging also demonstrates that the Ni distribution is zoned in the ApY(II) in irregular shaped bands subparallel with the contact between ApY(I) and ApY(II) (Figs. 3 and 6). However, EBSD analysis demonstrates that there are no differences in crystallographic lattice orientation associated with the change between ApY(I) and ApY(II) (Fig. 4) and therefore the crystal orientation did not affected the chemical composition of individual grains.

With respect to internal deformation of the arsenopyrite grains, Fougerouse et al. (submitted; Chapter III) demonstrated from EBSD data that both high-angle and low-angle boundaries are present in localised domains consistent with crystal-plastic deformation and limited arsenopyrite recrystallisation. This internal deformation is related to arsenopyrite grains affected by the S3Ob crenulation cleavage, (Fig. 4). In the example presented here (sample 215-20), a high density of crystallographic misorientations are localised in a narrow domain corresponding to the presence of ApY(II), adjacent to a large microfracture filled with undeformed (<2° misorientation) pyrite (Fig. 4). In this domain, the misorientations define low- and high-angle boundaries as well as new small grains. The geometry and position of the crystal-plastic misorientations, and associated low- and high-angle boundaries, correspond to greater surface areas of ApY(II) (up to three times more than in undeformed regions associated with ApY(II); Fig. 4). These observations suggest a link between crystal-plastic deformation within the arsenopyrite and loss of gold (see Fougerouse et al., submitted for further discussion).
5.3. Mineral-filled microfractures

The mineral-filled microfractures can be subdivided into two categories; (1) intragranular microfractures in arsenopyrites and (2) microfracture networks in folded quartz veins. The intragranular arsenopyrite microfractures can develop from grain boundaries and terminate within the arsenopyrite or entirely dissect the grains. They are usually filled with xenomorphic pyrite and chlorite, but also with native gold particles up to 10 μm across. Ankerite and quartz are not present. Importantly, Apy(II) forms semi-symmetric halos around the intragranular arsenopyrite microfractures. The pyrite within the intragranular microfractures has fine-scale Ni zoning and is usually Au-poor but contains native gold inclusions (Figs. 3, 5 and 6). Such Ni-enriched pyrite is referred to here as Py(III). The Py(III) is also developed in the intergranular regions between arsenopyrite grains and is in textural equilibrium with interstitial ankerite (Figs. 3 and 5).

Figure 6 shows an example of an intragranular microfracture cutting through an Apy(I) grain, including its gold-rich epitaxial zonation. This microfracture is infilled with Py(III) and bordered by a rim of Apy(II) before sharply transitioning to Apy(I). Au and Ni concentrations measured in a traverse from the microfracture to the centre of the grain (Fig. 6) confirm that the microfracture is filled with native gold grains and nickeliferous Py(III). The Au concentrations in the Apy(II) are below detection limit (XRF synchrotron; 400 ppm for this analysis), while the Apy(I) has gold concentrations up to 2000 ppm. In the Apy(II), close to the contact with the Apy(I), the Ni concentrations attain a maximum value of 2880 ppm.

The microfracture networks in the quartz veins (microfractures type 2) can be observed in hand specimen and are usually radiating from larger fractures that are parallel with the S3 Ob cleavage. They are particularly well developed in the hinges of the F3 Ob folds. Large native gold particles are exclusively hosted in the quartz microfractures, which was demonstrated using 3D mapping of gold distribution in a mineralised quartz sample by high-resolution X-ray computed tomography (Fougerouse et al., in press). Typically, these gold particles are several hundreds of micrometres across and up to several centimetres long. A polymetallic suite of accessory minerals is solely associated with the microfractures in the quartz veins and is not found in the wall rocks. These accessory minerals include galena, chalcopryrite, sphalerite, bouronite, boulangerite, tetrahedrite, aurostibine, löllingite, pyrite, arsenopyrite, and rare bismuth tellurides (Oberthür et al., 1994). Muscovites and chlorites also infill the microfractures. They are vein selvedge derived from wall rock fragments (Fig. 1D).
Fig. 2. Backscattered electron images showing internal arsenopyrite textures. (A) to (C) the Apy(I) grains are cut by Apy(II). Apy(II) has a brighter BSE response indicating higher average atomic mass (in this case enriched in arsenic); (D) late generation Py(III) postdating the arsenopyrites; (E) and (F) Arsenopyrite aggregates studied in further details in figures 3, 4 and 5. Native gold is present in microfractures in Apy or at grain boundaries.
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Table 1: Electron microprobe analysis of different domains of Apy in Wt%. BDL refers to “Below Detection Limit” (230 ppm). Modified from Fougerouse et al. (in press).
Fig. 3. Sample 215-7b arsenopyrite aggregate. (A) Synchrotron XFM RGB image (Red, Calcium; Green, Iron; Blue, Arsenic). The aggregate is composed of arsenopyrites with interstitial pyrites and ankerite. The matrix is composed of muscovite, chlorite and quartz; (B) Synchrotron XFM RGB image (yellow, gold; blue, nickel). The sulphides are gold-bearing arsenopyrites (Apy(I)) and Ni-rich pyrites (Py(III)). In Apy(I), the gold content is zoned with high concentrations in epitaxial overgrowth regions, whereas the cores are gold-poor. Nickel is enriched in both the interstitial Py(III) and the Apy(I) rims, parallel with microfractures and grain boundaries. The grain boundaries and Apy(I) are contoured in red. (C) to (H) NanoSIMS elemental maps of Apy zones indicated on (B). (C) and (F) $^{60}\text{Ni}^{32}\text{S}$ distribution; (D and (G) $^{197}\text{Au}$ distribution; (E) and (H) composite RGB image (yellow, $^{197}\text{Au}$; blue $^{60}\text{Ni}^{32}\text{S}$). Apy(I) rims are gold-poor and Ni rich. They cut across the fine, micron scale gold-rich oscillatory zoning of Apy(I), with sharp irregular boundaries. Native gold particles are located in a healed microfracture.
Figure 4: Arsenopyrite in crenulated phyllites (sample 215-20). (A) Backscattered electron image, the grain boundaries of Apy(I), Apy(II) and Py(III) are contoured in red. Position of figures (C), (D) and (E) are indicated; (B) Coloured EBSD map showing crystallographic misorientations in the range 0-10° of arsenopyrite and pyrite. Subgrains developed in the arsenopyrite are marked in black. The pyrite remains undeformed. There is no change in crystallographic orientation where Apy(I) changes to Apy(II), including preservation of the zones of crystal-plastic deformation. (C) NanoSIMS map of $^{60}$Ni$^{32}$S showing nickel distribution; (D) NanoSIMS map of $^{197}$Au; (E) NanoSIMS composite RGB image (yellow, $^{197}$Au; blue $^{60}$Ni$^{32}$S). The Apy(II) is gold-poor and crosscuts the fine, micron scale gold-rich oscillatory zonation of the arsenopyrites. Ni-rich Py(III) is located in the healed microfracture and the width of Apy(II) is up to 3 times greater in the areas associated with high densities of misorientation observed on (B).
Fig. 5. Sample 215-7b arsenopyrite aggregate 2. (A) Synchrotron XFM RGB image (Red, Calcium; Green, Iron; Blue, Arsenic). The aggregate is composed of arsenopyrites with interstitial pyrites and ankerite. The matrix is composed of muscovite, chlorites, ankerites and quartz; (B) Synchrotron XFM RGB image (yellow, gold; blue, nickel). The sulphides are gold-bearing arsenopyrites (Apy₁), with small replacement zones of Ni-rich arsenopyrite (Apy₁₁) and Ni-rich pyrites (Py₁₁₁). In Apy₁, the gold concentration is zoned with higher concentration in epitaxial overgrowth whereas the cores are gold-poor. The grain boundaries and Apy₁₁ are contoured in red. Position of NanoSIMS elemental maps are indicated (Fig. 6); (C) Au and Ni concentrations along the A-A’ traverse. In the microfracture labelled in (A), the high Au and Ni values reflect the presence of native Au and Py₁₁₁. The Au concentration is below detection limit in the Apy₁₁ while the Ni distribution show an edge of high concentration near the sharp contact with Apy₁. In Apy₁, Au concentrations attain 2000 ppm, whereas the Ni concentrations decrease from approximately 750 ppm to below detection limit toward the centre of the grain.
Fig. 6. NanoSIMS elemental maps of Apy zones indicated on figure 4. (A) and (B) composite RGB image (yellow, $^{197}$Au; blue $^{64}$Ni$^{32}$S). The Apy$_{(III)}$ is gold-poor and cuts across the fine, micron scale gold-rich oscillatory zoning of Apy$_{(I)}$. Native gold particles are located in a healed microfracture.
6. Discussion

6.1. Interpretation of mineral textures timing relationships and mass balance estimates

From the overprinting textural relationships, a clear sequence of events can be determined at the mineral scale with respect to Au mineralisation. (1) The fine-scale oscillatory zoning within Apy(I), defined by Au concentration (Fig. 3D and E), developed first. This is interpreted to reflect crystallographic interface and growth-rate-controlled incorporation into the crystal lattice of primary arsenopyrite developed during an initial hydrothermal event (Barker and Cox, 2011; Barker et al., 2009; Chouinard et al., 2005), rather than variations in fluid composition deriving from multiple separate hydrothermal events, which would have also led to major chemistry changes between different bands (Barker et al., 2009). (2) Apy(II) cuts across the epitaxial zones of Apy(I) and, therefore, postdates Apy(I) (Fig. 2A-C). This nickeliferous Apy(II) is spatially associated and coeval with Ni-bearing Py(III) and native Au located in the intragranular arsenopyrite microfractures. Py(III) is also intergrown, and is, therefore in textural equilibrium with late-stage ankerite that fills fractures and spaces between Apy grains (Fig. 3A). (4) Because the dimensions of Apy(II) are enhanced by the presence of sub-grains and intragranular microfractures formed during D3Ob, it is interpreted that Apy(II), Py(III), native Au and the interstitial ankerite developed at the later stages of the D3Ob deformation event. A second generation of chlorite overgrew the S3Ob cleavage and would have also formed during this late Au mineralisation event (Fougerouse et al., in press). Quartz is notably absent from the microfracture networks that host remobilised Au, suggesting that silica was undersaturated in the fluid phase.

Although truly quantitative 3D calculations were not achievable, we estimated the quantity of Au remobilised from individual arsenopyrite grains using 2D surface area calculations. In individual images, the surface area of the Apy(II) was measured (average of 15% of the total grain surface) and the quantity of Au removed was calculated based on an average concentration for Apy(I) of 1000 ppm (Fisher et al., 2014; Fougerouse et al., in press). The surface areas of the native Au particles were similarly measured and the quantity of Au estimated based on the assumption that they are 100% Au (i.e., a maximum estimate). It was found the native Au in fractures amongst arsenopyrite represents only 30-70 % of the Au extracted from the arsenopyrites. Therefore, on average 750 ppb of Au was extracted from arsenopyrite per tonne of rock, with between 525 and 225 ppb of Au migrating out of the system at distances greater than the scale of the petrographic thin-section (4 cm).
6.2. Gold remobilisation from arsenopyrite grains

Several characteristics enable us to distinguish the mechanism responsible for Au mobilisation from arsenopyrite. Firstly, the Apy(I) morphology and its crystal lattice orientation are preserved across Apy(I)–Apy(II) boundaries and there is a compositional difference between the two arsenopyrite types, with Apy(II) containing lower S and higher As content. Secondly, native Au in the intragranular microcracks within arsenopyrite is neither associated with clusters of sulfosalts, tellurides, sulphides and native metals, nor curved phase boundaries. Finally, the boundary between Apy(I) and Apy(II) is sharp, suggesting intragrain diffusion was not the predominant mechanism for Au remobilisation.

Given that Au can be mobile in a polymetallic melt at temperatures well below 340°C (Cockerton and Tomkins, 2012; Oberthür and Weiser, 2008; Tomkins et al., 2004), and that the metamorphic peak reached 340 - 460°C, we will briefly consider the possibility that some Au was mobilised as a molten sulphide phase. In the system Fe–As–S, the first melt can appear at temperatures as low as 281°C (Frost et al., 2002), but only when the sulfur fugacity is high and beyond the arsenopyrite stability field (Tomkins et al., 2004), which is clearly not the case at Obuasi. The polymineralic accumulations containing Au in the quartz veins (Fig. 1F) are reminiscent of the textures formed by crystallisation of Au-bearing polymetallic liquids, but the phase relations in the relevant system (Au-Sb-As-Pb-Cu-Fe-S) suggest that the assemblage would have been solid at the peak metamorphic conditions (see Tomkins et al., 2004). At these temperatures and fS2 conditions necessary to stabilise arsenopyrite, the system would need to contain native bismuth or mercury at low fS2, or thallium as part of the sulfosalt assemblage (cf. Tooth et al., 2008; Tomkins et al., 2004); however, such phases are not present. Therefore, we find that at Obuasi, it is unlikely that a Au-rich polymetallic melt ever developed.

Instead, our evidence indicates the dominant mechanism was pseudomorphic replacement of arsenopyrite by fluid-mediated dissolution-reprecipitation (Borg et al., 2014; Corfu et al., 2003; Geisler et al., 2007; Harlov et al., 2005; Putnis, 2009). In this case the relevant reaction is:

$$\text{Au}_x\text{Fe}_{1-x}\text{AsS}_{\text{high S}} + \text{NiCl}_2\text{(aq)} + 2\text{H}_2\text{O}\text{(aq)} + e^- \rightarrow \text{Ni}_y\text{Fe}_{1-y}\text{AsS}_{\text{low S}} + \text{Au(HS)}_2^-\text{(aq)} + 2\text{HCl}\text{(aq)} + \text{O}_2 \quad [1]$$

Where “x” and “y” represent the trace element concentration of Au and Ni, respectively. Geochemical modelling generated using Geochemist’s Workbench software (Bethke, 2008) and thermodynamic properties from the HCh database (Shvarov, 2008; Shvarov and Bastrakov, 1999) supports this interpretation and enables us to constrain the fluid chemistry. Figure 7 shows the activity diagram for the predominant speciation of Au and Ni at 350 °C,
Fig. 7. pH-Eh activity diagram for the predominant Au (A) and Ni (B) speciation at 350 °C, 2k bar. The solution contains Cl⁻ (α=0.065), SO₄²⁻ (α=0.03), Fe²⁺ (α=0.01), and 1ppb-10ppm amount of Au⁺ or Ni²⁺. The dashed blue lines show the boundary of different sulfur species, the dashed green lines show the field of Fe minerals as redox buffer. The solid red line and yellow line indicate the boundary of the predominant Au or Ni species (with 1 ppb to 10 ppm Au or Ni in the solution the thick, red to yellow dash lines). The pentlandite stability field represents the domain that Ni is predominantly stable as a solid sulphide mineral phase (arsenopyrite in our case study).
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2 kbar as a function of pH and oxygen fugacity. As shown in Figure 7, the concentration of Au in solution can reach anomalous values, up to 10 ppm at pH = 6 to 7 and log\(O_2\) = -32 to -28, near the pH of HS⁻/H₂S equivalence point and the pyrite-pyrrhotite redox buffer, which is 1-3 orders of magnitude more than expected for orogenic systems (Mikucki, 1998) and 3 orders of magnitude more than measured in deep, Au-rich geothermal fluids (Simmons and Brown, 2007). At the same pH and redox conditions, Ni is predominantly stable as a solid sulphide mineral phase (Fig. 7). The loss of sulphur associated with Ni replacement of Fe in arsenopyrite (Table 1) is critical because it increases the solubility of Au as a Au(HS)₂⁻ complex (Liu et al., 2014) at the crystal-fluid interface, promoting liberation of Au from the solid phase and remobilisation. The reaction model also shows that at increasing \(fS_2\), Ni precipitates whereas Au dissolves in the solution (Fig. 8). This may be coupled with the apparent tendency of Ni to inhibit accommodation of Au in the arsenopyrite structure (i.e., based on our observations), which if true, would also promote remobilisation. Such a possibility can be addressed by considering how Au and Ni are substituted into the arsenopyrite structure. Along with a proportion of nanoparticulate Au, it is thought that Au⁺ substitutes to a small extent (a few thousand ppm) for six-fold coordinated Fe³⁺ in arsenopyrite (see summary of previous work in (Cabri et al., 2000), although there may be some nonsystematic incorporation into lattice defects (Reich et al. 2005). It should be noted that the nature of Au substitution in arsenopyrite is still not well understood and XAS and x-ray crystallography studies indicate that the bonding environment of Au in arsenopyrite is complex. In contrast, there is complete solid solution between FeAsS and NiAsS (gersdorffite), as well as CoAsS (cobaltite). The ionic radii of six-fold coordinated Fe³⁺ and Ni³⁺ are 0.785 and 0.74 Å, respectively (Co³⁺ is 0.75 Å), whereas that of Au⁺ is 1.51 Å (Shannon, 1976), so Au does not fit as easily into the arsenopyrite structure as Ni. Similarly, the difference in ionic charge of Au to that of Ni (and Co) relative to Fe, implies that Ni should be preferentially substituted for Au in arsenopyrite. It should, therefore, be expected that both Ni and Co would preferentially replace Au in the arsenopyrite crystal structure if they became available via a later fluid. In regards to Au in lattice defects, it may be that the Ni replacement process heals defect structures, leaving Au more susceptible to fluid complexation.

One of the interesting features of the system studied here is that there no quartz precipitation during remobilisation of the Au into the microfracture networks in quartz, requiring that the fluid was SiO₂ undersaturated. Fundamentally, decreasing temperature causes a decrease in SiO₂ solubility in H₂O, so fluids infiltrating from a hotter source region below should tend to precipitate quartz. Nonetheless, typical orogenic fluids are not pure H₂O, and at any given temperature SiO₂ solubility varies as a function of H₂O activity.
Fig. 8. Impact of the addition of sulphur to the fluid by changing $\log f_S^2(g)$ from -15 to -6 at 350 °C, 2k bar (e.g. as the arsenopyrite replacement reaction occurs sulphur is released). The initial reactant contains 1 kg $H_2O$, 1 molal $Cl^-$, $10^{-4}$ molal $Ni^{2+}$, $10^{-3}$ molal $Fe^{2+}$, 1 g native gold, 1 g arsenopyrite and some $Na^+$ to balance the charge. The pH is fixed at 7 and the initial $log f_O^2$ of -33 is chosen for the reaction. (A) The total amount of Ni and Au in the solution. (B) The stable mineral phases as the reaction proceeds.
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Figure 9. Reaction removing CO₂ from the fluid as carbonate precipitates. Temperature of 350 °C, 2k bar containing 1 kg H₂O, 1 molal H₂S(aq), 1 molal Cl⁻, 10⁻⁴ molal Ni²⁺, 10⁻³ molal Fe²⁺, 1 g native gold, 10 g quartz, 1 g calcite and some Na⁺ to balance the charge. The pH changes from 5.7 to 8 as the reaction proceeds, and log fO₂ changes from -28.9 to -30, depending on the amount of CO₂ in the system. (A) The total amount of Au and Si dissolved in solution as CO₂ is removed from the fluids; (B) Change of pH and oxygen fugacity during reaction; (C) Concentration of important sulfur speciation and the total sulfur concentration in the fluids.
Since quartz is relatively insoluble in CO₂ (Newton and Manning, 2000; Shmulovich et al., 2001), quartz solubility will decrease with increasing XCO₂. The late fluid responsible for Au remobilisation was likely to have been a typical orogenic H₂O–CO₂–H₂S fluid that had equilibrated with regional rocks, and thus was quartz-saturated or even supersaturated upon infiltration. However, precipitation of the intergranular ankerite would have removed CO₂ from the fluid, necessitating an increase in the solubility of quartz in the fluid, thus inhibiting quartz precipitation and possibly even facilitating some quartz dissolution. An additional consequence of this process is that by removing CO₂ from the fluid, the relative abundance of H₂S increases thereby further enhancing the solubility of Au and buffering the fluid chemistry towards the ideal pH conditions for Au dissolution.

We calculated the effect of removing CO₂ from the Au and Si rich system. The solubility of Si has potential to increase from 500 to 3000 ppm during the removal of CO₂, especially in the range of 2 – 0 wt% of CO₂ in fluids; quartz is rapidly dissolved with a corresponding pH change from 7-8 (Fig. 9). The solubility of Au increases from 400 to 800 ppm when CO₂ content decreases to 5 wt% in the fluids; however, the Au solubility drops to ~20 ppm when CO₂ is totally removed. The decrease of Au solubility by about two orders of magnitude corresponds to the change of pH from 6.8 to 8, which is consistent with the activity diagram shown in Figure 7. The pH changes from 5.7 to 8, when removing CO₂, crosses the HS-/H₂S equivalence point, whereas fO₂ changes in a very narrow range and stays in the pyrite stability field (log fO₂ = -30 ~ - 28.9). The total sulphur content in the fluid increases through the reactions and controls the Au carrying ability of the fluid. The preferred pH range condition for Au mobility is 6-6.8 (neutral conditions), whereas Si is more mobile at neutral to alkaline conditions (>6.5). An important conclusion is that moderation of XCO₂ through carbonate precipitation can control both Au remobilisation and Si solubility in H₂O-CO₂ fluid systems.

Two observations indicate that only a low volume of fluid percolated through the metasediments during arsenopyrite replacement and Au remobilisation. Firstly, the primary silicate alteration mineral is chlorite, which overprints S₃ Ob, yet there has been only minor new chlorite formation in the host metasedimentary rocks close to the quartz veins. Secondly, the arsenopyrites have only been partially replaced in some places, whereas this process would have been pervasive if large volumes of fluid had pervaded during D₃ Ob. Given the locally very-high concentrations of Au in some fractures, and the low volume of fluid infiltration, the remobilising fluid must have been characterised by very high Au in solution. Such a fluid would be fundamentally different to the large volume and comparatively dilute fluids usually associated with hydrothermal orogenic Au deposits (McCuaig and Kerrich, 1998; Micklethwaite et al., 2015; Mikucki, 1998). In our model, this
Fig. 10. Interpretation of arsenopyrite alteration, metal remobilisation and native gold precipitation in fracture networks and quartz vein fold hinges. (A) The arsenopyrite-hosted mineralisation is equally distributed along the strike of the veins. The highest gold grades and native gold are hosted in the F3$_{ob}$ fold hinges of the quartz vein. (B) Partial crystal-plastic recrystallisation of the arsenopyrites was synchronous with D3$_{ob}$ (Fougerouse et al. in press). This microstructure and intragranular microfractures allowed fluid infiltration and psuedomorphic replacement of Au-rich Apy with Ni-rich but Au-barren Apy. Psuedomorphic replacement also occurred on undeformed boundaries of the grains. Ni-rich pyrite crystallised synchronously in intragranular microfractures; (C) Low volume Ni-bearing fluid migrated pervasively in the wall rock, along the S3$_{ob}$ cleavage planes, grain boundaries and microfracture networks, facilitating reaction and leading to release of gold and S into the fluid; (D) Native gold precipitates in fracture networks in the previously formed quartz veins, as well as microcrack networks in the wall rock to a lesser extent.
attainment of unusually high-Ausolubility conditions for Au was facilitated by three processes that occurred at the sites of pre-existing Au mineralisation: (1) replacement of Au-rich arsenopyrite by Au-free and Ni rich arsenopyrite liberated Au whilst simultaneously increasing the amount of sulphur available for Au complexation at the crystal-fluid interface, (2) precipitation of ankerite removed CO₂ from solution, increasing the proportion of sulphur in solution and thus Au solubility, and (3) ankerite precipitation buffered fluid pH towards the ideal conditions for maximising Au solubility, near the H₂S–HS⁻ equivalence point of 6 - 6.8 (Figs. 7, 9).

The subsequent loss of sulphur from the fluid, as pyrite precipitates in the microcracks, acted to lower Au solubility and promote re-precipitation of Au. Such interactions explain why there is an association between Au and pyrite in fractures in arsenopyrite and why remobilisation can occur over short length-scales. Nonetheless, as long as some sulphur remains in the fluid, Au can also be mobilised greater distances. Therefore, we suggest that the Au found in the microfracture networks in deformed quartz veins was derived from the Au-bearing arsenopyrite, implying remobilisation distances exceeding several tens of meters as the fluids evolved to higher sulphur content through reaction (Fig. 10). The fluid migrated along cleavage planes, grain boundaries and wall rock microfractures to the quartz veins. Folding and fracturing of the quartz veins established an interconnected microfracture network and created a hydraulic gradient, causing fluids to migrate into the microfractures in quartz vein fold hinges, where high grade oreshoots ultimately developed (Fig. 10).

6.3. Global Implications

Given that both Ni and Co can be transported as chloride species (Liu et al., 2011; Liu et al., 2012; Tian et al., 2012), typical orogenic fluids, which have 3-7 wt.% NaCl equivalent (Ridley and Diamond, 2000), should be capable of providing sufficient quantities of these metals to cause the observed replacement at Obuasi and elsewhere. However, these metals are not evenly distributed in the crust, so the late-stage fluid would need to interact with some mafic or ultramafic material in which these metals are considerably more abundant. These rock types are relatively abundant in Archean and Proterozoic crust, so this process of late-stage remobilisation may be common to many Au deposits. Indeed, Au is found in fractures in arsenopyrite at numerous occurrences around the world (Cook et al., 2013; Essarraj et al., 2001; Morey et al., 2008; Mumin et al., 1994), and in the few cases where trace element concentrations of Ni and Co have been measured, it can be seen that there are late Ni and/or Co rich overgrowths on arsenopyrite and adjacent Au in fractures (e.g., Fig. 6 in Cook et al., 2013; Fig.7 in Morey et al. 2008).
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7. Conclusions

In the Obuasi Au deposit, interaction between an early generation of Au-bearing arsenopyrite and a later generation of low volume, relatively low fS2 fluid, carrying aqueous NiCl2, initiated replacement reactions in arsenopyrites and liberated Au in solution. During this reaction, liberation of sulphur from the arsenopyrite and precipitation of ankerite increased the solubility of Au and silica significantly, allowing Au to be transported over distances exceeding 50 m. The folding and fracturing of the quartz veins drove the fluid migration into and through the fold hinges of the quartz veins and promoted precipitation of polymetallic sulphides and native Au in the fracture network of the quartz veins.

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Geometry and genesis of the giant Obuasi gold deposit, Ghana

1. Key research outcomes

This study provides results across multiple scales and integrates analytical approaches that cover the macro to micrometer scales (SIMS, NanoSIMS, X-ray Fluorescence Synchrotron, SEM, EPMA, optical microscopy and 3D X-ray microscopy), to open pit and drive scales (mapping, structural analysis), to deposit scales (Leapfrog 3D visualisation). A wide range of tools and methodologies were integrated in the common objective of unravelling the processes that occurred during the formation of the biggest gold deposit of West Africa. The main outcomes are summarised below.

1.1. A new deformation scheme

The rocks at Obuasi are strongly deformed and a multistage deformation history has been identified (Blenkinsop et al., 1994; Allibone et al., 2002; Fougerouse et al., in press; Chapter II) with differences and contradictions amongst models most notably the deformation sequence. Based on new field data and the reassessment of previous data, we demonstrated that the structures and foliations define a three stage sequence.

The oldest fabric (S1_{ob}) recorded is poorly preserved and has a small angle with respect to the bedding (S0). S1_{ob} is folded and transposed by later structures and fabrics (Allibone et al., 2002).

The dominant foliation in Obuasi (S2_{ob}), strikes northeast and dips steeply southeast to northwest, is axial planar to and formed coeval with the northeast plunging F2_{ob} isoclinal folds. The main S2_{ob} cleavage is interpreted to be the result of a NW-SE directed shortening...
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(D2_{Ob}). The major faults and shear zones in the district share the same orientation as S2_{Ob} and were interpreted to form during D2_{Ob}. The large quartz veins hosting the visible mineralisation also formed during D2_{Ob}. Subhorizontal stretching occurred during the late stage of D2_{Ob} with intense boudinage and the formation of quartz pressure shadows around sulphides and carbonates. This event represents a period where strain was accommodated by pervasive flattening and stretch, and localised high strain along shear zones (Fougeroue et al., in press). D2_{Ob} corresponds to D2 of Allibone et al. (2002) and D1 of Blenkinsop et al. (1994).

These fabrics are overprinted by a crenulation cleavage (S3_{Ob}) and coeval generation of folds (F3_{Ob}). The S3_{Ob} cleavage strikes east-northeast and dips shallowly to steeply to the north-northwest. F3_{Ob} fold axes plunge 20° to 50° to the northeast. D3_{Ob} corresponds to a NNW-SSE to N-S shortening direction and is similar to D4 of Allibone et al. (2002) and D2 of Blenkinsop et al. (1994).

In addition, Allibone et al. (2002) reported a flat-lying cleavage (named S3) that trends northeast, as well as mineralized quartz veins that were interpreted to form during late sinistral strike-slip displacement on shear zones. The significance of these fabrics is discussed in details in Chapter II and may reflect localised deformation occurring during D3_{Ob} rather than a distinct regional tectonic event.

### 1.2. Multistage mineralisation and alteration footprints

The relative timing of mineralisation at Obuasi has been much debated (Blenkinsop et al., 1994; Oberthür et al., 1994; Allibone et al., 2002; Fougeroue et al., in press). Allibone et al. (2002) previously interpreted all the gold mineralization to be coeval with a late sinistral reactivation of the Ashanti fault system, either post-dating or in the late stage of D3_{Ob}, whereas Oberthür et al. (1994) and Blenkinsop et al. (1994) interpreted the mineralisation to have occurred earlier during the main deformation event D2_{Ob}. However, we have documented a multistage mineralisation history (Chapter II).

The first stage of mineralisation at Obuasi occurred during NW-SE shortening (D2_{Ob}). This event is characterised by formation of gold-bearing arsenopyrites and thick quartz veins which precipitated along graphitic shears (fissures), while a carbonate alteration footprint (ankerite and siderite) developed and has an extent of 25-50 m from the edge of the ore zone. Evidence to support this model is based on strain shadows surrounding the gold-bearing arsenopyrite and carbonates. The strain shadows are parallel and formed during the development of the S2_{Ob} and were then crenulated by the S3_{Ob} cleavage.
The second episode of mineralisation during D3\textsubscript{Ob} corresponds to visible gold overprinting the quartz veins formed earlier, during D2\textsubscript{Ob}. The highest gold grades and the visible gold mineralisation are specifically located in fractures in the hinges of the F3\textsubscript{Ob} folds, as documented by micrometre-scale high-resolution X-ray computed tomography of quartz samples, underground mapping and deposit-scale 3D visualisation (Chapter II). A chlorite alteration halo overprinting the S3\textsubscript{Ob} cleavage is weakly developed around the high-grade quartz veins.

Although the two events defined by Fougerouse et al. (in press) are distinct, they both likely occurred during the Eburnean orogeny, with the early stage of mineralisation constrained by U/Pb zircon ages of the Anyankyerem granite (cut by mineralisation) to younger than $2106 \pm 2$ Ma (Oberthür et al., 1998).

1.3. Microstructural and chemical evolution of the gold-bearing arsenopyrites

In the Obuasi deposit, approximately half of the gold resource is locked in arsenopyrites disseminated in the wall rock. A strong focus of this study was to document the trace element distribution and microstructural evolution of the gold-bearing arsenopyrite during metamorphism and metasomatism.

The microstructural data (EBSD - Chapter III) give important insights on the behaviour of arsenopyrite during high strain deformation and metamorphism. Although the grains remain undeformed after D2\textsubscript{Ob}, we documented small amount of crystal-plastic deformation developed during D3\textsubscript{Ob}, at a high-angle to the arsenopyrite long axis. We conclude arsenopyrite is remarkably resilient to crystal plasticity at the recorded temperatures of 340° - 460° and pressures of 2 kbars of the Eburnean orogeny. Such robust properties for arsenopyrites contribute to our understanding of the ability of arsenopyrite to incorporate gold into its crystal lattice and, more importantly, its ability to preserve such precious metal concentrations through subsequent events in the rock record.

However, in a large proportion of the arsenopyrite grains, alteration rims were observed (Chapter V). The alteration rims cut across the primary oscillatory, sub-micrometre scale gold zonation of the arsenopyrites. Although these rims have a different composition (approximately stoichiometric, enriched in Ni), they preserve the original shape of the parent arsenopyrite crystal but have lost all their gold content. The alteration rims have all the characteristics of replacement zones described in pseudomorphic dissolution-reprecipitation reactions (Corfu et al., 2003; Harlov et al., 2005; Geisler et al., 2007; Putnis, 2009).

Importantly, where small amounts of crystal plasticity generated both low- and high-angle boundaries in the arsenopyrite during D3\textsubscript{Ob}, the replacement zones are up to 3 times
wider. This observation indicates that the reaction is enhanced by the presence of subgrains and neoblasts and likely had occurred syn- or post-D3ob.

Critically, contemporaneously with the replacement reaction and the extraction of gold from the arsenopyrite during D3ob, high-grade ore shoots formed with native gold overprinting the adjacent quartz veins. In this study we established that gold mineralisation occurred in two stages: the first as lattice-bound gold in the D2ob disseminated arsenopyrite and the second comprising D3ob high grade visible gold in quartz veins.

Consequently, we have argued that the native gold mineralisation during the second event could have been sourced from remobilisation of the gold-bearing arsenopyrite in the wall rock. Gold addition by another fluid from an external source cannot be ruled out, and further work is needed to investigate the proportions of gold sourced from the disseminated arsenopyrite and another hydrothermal fluid, if any.

2. Implications for exploration

Throughout the project, reports and presentations were delivered to the sponsor of this study, AngloGold Ashanti Ltd. Some of this information communicated remains confidential and cannot be reported in this thesis. However, this section provides an overview of the main outcomes for exploration;

- Harmonised pit and underground maps - each mineralized trend was studied in detail and lithological and structural maps were issued. The most important observation emerging from these maps is that the locations of the ore zones in all 3 trends are spatially associated with lithological contacts with contrasting competency. We suggest that developing a comprehensive 3D framework of the facies variations, intrusive architecture and lithological architecture of the Obuasi district would assist in identifying areas of major competency contrast through the Obuasi region;

- Individual high-grade ore shoots can be grouped into three categories on the basis of geometry and lithological controls. The first group corresponds to volcanic rock and dyke controlled shoots with inferred rheological contrasts controlling the gold distribution. The geometry of these ore shoots can be sub-vertical or gently plunging to the northeast at <20°. The second group consists of ore shoots that have variable trends and can be either sub-horizontal, steeply dipping or even southeast-plunging (the opposite to the dominant northeast ore shoot plunge). This group is related to fault intersections and splays - the variable ore shoot plunges are a function of the
different strikes and dips of the intersecting faults. The dominant and third ore shoot group at Obuasi plunge moderately to the northeast at 20° to 40° and are associated with late F3 ob fold hinges and the S3 ob cleavage intersection with the Ashanti fault plane. Many ore shoots are hybrid systems with more than one of the above controls.

The identification of the ore shoot geometry has led to a better understanding of the controls on mineralisation which can be integrated into the Brownfield exploration strategies;

- A new leapfrog 3D structural model was used to visualise the gold and lithological distribution. Using this 3D model integrated with detailed field mapping and the other results of this study, six near mine targets were identified for the Obuasi exploration team for testing. These targets are distinct to the ongoing exploration strategy of targeting the extensions at depth of the existing group 3 ore shoots. Three of these targets are suggested as high priority as they represent important near-surface ore-deposit potential;

- The mineral paragenesis and mineral chemistry changes associated with hydrothermal alteration and mineralisation are identified. The carbonate halo has been identified as the footprint of the Au-bearing arsenopyrite mineralisation, whereas a weak chlorite footprint surrounds the native gold mineralisation. Major element CO3 and hyperspectral analysis of chlorites and carbonates chemistry may have potential as vectoring tools to improve targeting of mineralisation during regional exploration;

3. **Further work**

In this study, we used a combination of conventional and novel techniques to investigate the geometry and genesis of the Obuasi gold deposit. Although we have made great progress in the understanding of the deposit, there are still some remaining questions which are of particular interest for the author of this thesis;

- The dominant ore shoot geometry (group 3) is controlled by D3 ob structures. However, a significant proportion of the total gold resource is hosted in arsenopyrites disseminated in the metasedimentary rocks and formed earlier, during D2 ob. It is suggested that competency contrasts between rock types could control the formation
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of the arsenopyrite ore shoots. However, defining the geometry of such ore shoots could become critical for exploration purposes;

- Mass balance estimations in Chapter V demonstrated that gold was liberated by the arsenopyrites. However, during this study, the gold contained in the quartz veins could not be physically traced back to the disseminated arsenopyrites in the sedimentary rocks and further work is needed to test this hypothesis. In order to investigate this further, potentially two paths could be followed; the first one using in situ stable or radiogenic isotopes and the second to determine the nickel distribution between low- and high-grade alteration zones to trace the fluid pathway responsible for the gold remobilisation during D3_{OB};

- In Chapter V, we discuss the physio-chemistry properties of the fluid suspected to be responsible for the remobilisation of large quantities of gold and reprecipitate them in adjacent quartz veins. A fluid inclusion study on the phases linked with the D3_{OB} event, for example, the Ni-rich pyrites and the accessory minerals hosted in the fractures of the quartz veins, could potentially better constrain the chemistry, pressure-temperature and pH of this fluid. Techniques such as infrared light microthermometry, Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), Synchrotron Radiation-induced X-Ray Fluorescence (SR-XRF) and X-ray Absorption Near Edge Structure (XANES) experiments would allow characterisation of the fluid responsible for the formation of opaque minerals (Cauzid et al., 2007; Kouzmanov et al., 2010);

- In Ghana the Ashanti and Akropong faults host numerous large gold deposits, including Prestea (11 Moz), Bogoso (4 Moz), Konongo (3 Moz), Ayanfuri (1 Moz) and Pampe (200,000 oz) with similarities in host rocks and mineralisation styles. Although several studies documented the geology of these deposits (Dzigbodi-Adjimah, 1993; Mücke and Dzigbodi-Adjimah, 1994; Mumin et al., 1994; Mumin et al., 1996; Oberthür et al., 1997; Allibone et al., 2002a; Feybesse et al., 2006; Perrouty et al., 2012), the preferred model for the formation of these deposit is that only one mineralisation event occurred. It would be valuable for the understanding of the metallogenical processes involved in the well-endowed Ashanti belt to re-investigate the absolute timing of mineralisation and ore shoot geometries in other deposits to compare with Obuasi. This re-evaluation could help exploration strategies and potentially explain the extreme size of the Obuasi deposit. Gold remobilisation has also been documented in the Bogoso-Prestea mining district (Mumin et al., 1994),
suggesting that remobilisation occurred across the deposit hosted in the Ashanti belt. Regionally, other publications in preparation by WAXI research collaborators documented remobilisation evidence in the Inata gold deposit, northern Burkina Faso (McCuaig et al., in press).

4. References


Chapter VI: Conclusion


Appendix I: Ores and alteration mineral petrography
Appendix I: petrography

Introduction

This appendix provides further information and images acquired during the petrographic and mineralogical work. The first part (I) details the petrography of the hydrothermal alteration phases. The second part (II) expands the ore mineralogy of the quartz vein ores. Strain fabric characterisation, mineral identification, mineral chemistry zonation, overprinting relationships and paragenesis were investigated with a combination of optical techniques and scanning electron microscopy (SEM).

I. Alteration assemblage petrography

To characterise the alteration footprint of the Obuasi deposit, samples were collected across a mineralised zone as well as further away from the mineralisation. Strain fabric characterisation, mineral identification, mineral chemistry zonation, overprinting relationships and paragenesis were investigated with optical techniques and scanning electron microscopy (SEM).

This section provides additional images to the thesis acquired during petrography.
**Figure 1: Electron backscattered image**

<table>
<thead>
<tr>
<th>Sample number</th>
<th>318-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample location</td>
<td>Level 30#1 Cross-cut 318</td>
</tr>
<tr>
<td><strong>Observation</strong></td>
<td>Carbonate minerals (Ankerite and siderite) are aligned with the S2 cleavage. The matrix is composed of quartz, muscovite and chlorite.</td>
</tr>
<tr>
<td><strong>Interpretation</strong></td>
<td>The carbonates, aligned with S2, precipitated during the development of the cleavage, i.e. during D2.</td>
</tr>
</tbody>
</table>
Appendix I: petrography

**Figure 2: Electron backscattered image**

<table>
<thead>
<tr>
<th>Sample number</th>
<th>318-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample location</td>
<td>Level 30#1 Cross-cut 318</td>
</tr>
<tr>
<td>Observation</td>
<td>Ankerite porphyroblasts are aligned with the S2 cleavage. Numerous inclusions of mainly quartz are preserved in the mineral. The matrix is composed of quartz and muscovite.</td>
</tr>
<tr>
<td>Interpretation</td>
<td>The ankerites, aligned with S2, precipitated during the development of the cleavage (i.e. during D2), though mimetic overgrowth cannot be ruled out.</td>
</tr>
</tbody>
</table>
### Observation
Ankerite porphyroblasts are aligned with the S2 cleavage. The ankerite is partially replaced by chlorite minerals. The matrix is composed of quartz, muscovite and chlorite.

### Interpretation
A second episode of alteration and a second stage of chlorite growth is preserved here. During this alteration ankerite was no longer stable and was partially replaced by the late chlorite.
Appendix I: petrography

Figure 4: Electron backscattered image

<table>
<thead>
<tr>
<th>Sample number</th>
<th>215-22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample location</td>
<td>Level 30#2 Cross-cut 215</td>
</tr>
<tr>
<td>Observation</td>
<td>The chlorite replaced most of the ankerite in this sample as well as overgrowing the S3 cleavage. The matrix is composed of quartz, muscovite and chlorite.</td>
</tr>
<tr>
<td>Interpretation</td>
<td>The chlorite minerals are aligned with both S2 and S3 cleavages indicating a stage of precipitation during both cleavage forming events i.e. syn-D2 and syn-D3.</td>
</tr>
</tbody>
</table>
**Sample number** | 318-11  
**Sample location** | Level 30#1 Cross-cut 318  
**Observation** | The chlorite porphyroblasts overprint S2 and S3. The gold-bearing arsenopyrites are aligned with S2. Their strain shadows are parallel with S2 and folded by S3. The matrix is composed of quartz, muscovite and chlorite.  
**Interpretation** | The gold-bearing arsenopyrites precipitated during D2 while the chlorite porphyroblasts are best syn- to post-D3.
Appendix I: petrography

Figure 6: Electron backscattered images

<table>
<thead>
<tr>
<th>Sample number</th>
<th>215-7b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample location</td>
<td>Level 30#2 Cross-cut 215</td>
</tr>
<tr>
<td>Observation</td>
<td>Left images are normal contrast and right images are high contrast optimised to observe textures in arsenopyrites. The pyrites overgrow the arsenopyrites. Trails of gold inclusion in the pyrite. Alteration rims in arsenopyrites in contact with pyrite.</td>
</tr>
<tr>
<td>Interpretation</td>
<td>The gold was extracted from zones around microfractures and grain boundaries. In these zones, gold was replaced by nickel. During this replacement a second generation of Ni-rich pyrite precipitated. During the gold remobilization, nickel replaced gold in the arsenopyrites and nickel-rich pyrites crystallised.</td>
</tr>
</tbody>
</table>
Appendix I: petrography

Summary:

The host rock is mainly composed of quartz-muscovite-carbonates ± albite. Several generations of alteration minerals can be observed depending on the proximity to the ore and overprinting relationships with host rock fabrics. In general, the alteration in the Obuasi district is remarkable in that the visual signature is restricted to only several tens of metres from the ore zones and does not have a particularly large footprint for such a massive ore deposit.

*Early syn-D2 carbonate alteration*

The first generation of hydrothermal minerals, aligned with S2\textsubscript{ob} are composed of ankerite and siderite (Fig. 1, 2 and 3). The proximal to intermediate alteration halo is characterised by the presence of ankerite and extends for several tens of meters around the mineralisation. This alteration assemblage is associated with arsenopyrite mineralisation aligned with S2\textsubscript{ob}.

The paragenetic relationships between these minerals indicate that ankerite and siderite are replaced by chlorite.

*Late D3 overprinting chlorite alteration*

A second stage of alteration is associated with chlorite overprinting the S3\textsubscript{ob} cleavage in close proximity to high grade ore in the folded quartz veins (Fig. 4 and 5). As the visible gold mineralisation is associated with D3\textsubscript{ob}, it is interpreted that the overprinting chlorites represent the proximal alteration of this ore.

In summary the alteration is characterised by two distinct assemblages:

- Broad ankerite/siderite hydrothermal alteration occurring during D2\textsubscript{ob} contemporaneous with the arsenopyrite mineralisation;
- Overprinting chlorites in close proximity of the high-grade lodes occurring during D3;
- Both alteration halos have the potential to be identified by hyperspectral methods or geochemistry and thus represent vector tools toward gold-bearing sulphide and/or high-grade visible gold mineralisation.
Appendix I: petrography

II. Quartz vein ores petrography and textures

To characterise the ore mineralogy of the Obuasi high-grade samples (i.e. visible gold in quartz veins), samples were collected from underground exposures and drill cores. Strain fabric characterisation, mineral identification, mineral chemistry zonation, overprinting relationships and paragenesis were investigated with optical techniques and scanning electron microscopy (SEM). To investigate the 3D distribution and geometric relationships of the native gold in the quartz veins, a 25 mm core of a high-grade quartz sample was scanned using the 3D X-ray microscope, installed at the Australian Resource Research Centre (CSIRO, Kensington).

This section will provide additional images to the report acquired during the petrography work.
**Sample number**  
DF034

**Sample location**  
Level 17 Cross-cut 394

**Observation**  
Quartz vein sample. Gold and accessory minerals hosted in microfracture of the quartz vein. The ore mineralogy is composed of gold, aurostibinite, chalcopyrite, sphalerite, tetrahedrite and bournonite. The matrix is composed of quartz mainly with minor ankerite and muscovite filling the fractures.

**Interpretation**  
The gold and accessory minerals are filling the quartz microfractures along with muscovite indicating that the quartz vein was overprinted by the mineralizing event.
Appendix I: petrography

Figure 8: Electron backscattered image

| Sample number | DF034 |
| Sample location | Level 17 Cross-cut 394 |
| Observation | Quartz vein sample. Gold and accessory minerals hosted in a microfracture of the quartz vein. The ore mineralogy is composed of Aurostibinite, chalcopyrite and tetrahedrite. The matrix is composed of quartz mainly with minor ankerite and muscovite filling the fractures. |
| Interpretation | The gold and accessory minerals are filling the quartz microfractures along with muscovite indicating that the quartz vein was overprinted by the mineralising event. |
Appendix I: petrography

Figure 9: Electron backscattered image

<table>
<thead>
<tr>
<th>Sample number</th>
<th>DF099</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample location</td>
<td>Level 29 Cross-cut 317</td>
</tr>
<tr>
<td>Observation</td>
<td>Quartz vein sample. Gold and accessory minerals hosted in the microfracture network of the quartz vein. The ore mineralogy is composed of gold, bournonite, tetrahedrite and arsenopyrite. The matrix is composed of quartz mainly with minor ankerite.</td>
</tr>
<tr>
<td>Interpretation</td>
<td>The gold and accessory minerals are filling the quartz microfractures network indicating that the quartz vein was overprinted by the mineralising event.</td>
</tr>
</tbody>
</table>
Appendix I: petrography

<table>
<thead>
<tr>
<th>Sample number</th>
<th>DF099</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample location</td>
<td>Level 29 Cross-cut 317</td>
</tr>
</tbody>
</table>

**Observation**
Quartz vein sample. Gold and accessory minerals hosted in the microfracture network of the quartz vein. The ore mineralogy is composed of gold, bournonite, tetrahedrite and pyrite. The matrix is composed of quartz mainly with minor ankerite.

**Interpretation**
The gold and accessory minerals are filling the quartz microfractures network indicating that the quartz vein was overprinted by the mineralising event.
Appendix I: petrography

Figure 11: Electron backscattered image

Sample number | DF091
---|---
Sample location | Level 43#1 Cross-cut 169
Observation | Quartz vein sample. The gold is hosted in the cleavage planes of the muscovite and in the microfracture network of the quartz. The ore mineralogy is composed of gold only.
Interpretation | The gold precipitated in the existing muscovite cleavage planes and microfracture network and therefore overprints the quartz vein.
Figure 12: Electron backscattered image

<table>
<thead>
<tr>
<th>SEM HV: 20.9 kV</th>
<th>WD: 15.79 mm</th>
<th>VEGA3 TESCAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date(m/d/y): 06/30/13</td>
<td>SEM MAG: 714 x</td>
<td>100 μm</td>
</tr>
<tr>
<td>View field: 354 μm</td>
<td>Det: BSE</td>
<td></td>
</tr>
</tbody>
</table>

Sample number | DF091
Sample location | Level 43#1 Cross-cut 169
Observation | Quartz vein sample. Trails of gold inclusions converging towards a larger gold nugget.
Interpretation | This texture implies a fluid characterised by very high gold concentration with possible gold being transported as nanoparticles.
Summary:

The quartz vein ores represent extremely high grade, visible gold mineralisation, as shown by the high-resolution X-ray computed tomography (Chapter II). SEM analyses indicate that the gold is distributed along fracture planes that crosscut the quartz veins rather than disseminated throughout the quartz vein (Figs. 7 to 12). The gold particles are flake-shaped with variable sizes filling the porosity of the quartz created by the fracturing. Native gold is associated with muscovite and graphite, but also galena, chalcopyrite, sphalerite, bournonite, boulangerite, and aurostibine as accessory minerals (Oberthür et al., 1994). The minerals are typically xenomorphic and can reach several hundred micrometres in size. The mutual intergrowths of these minerals indicate synchronous deposition (Oberthür et al., 1994). Further mineralogical and chemical results, as well as the interpreted ore mineral paragenesis, can be found in Oberthür et al., (1994).

The petrography results, along with the other arguments presented in the report, indicate that the visible gold mineralisation in the main Obuasi mine occurred during D3_{Ob} and overprints the quartz veins and the sulphide mineralisation.
Appendix II:

The Obuasi gold deposit, Ghana: A West African giant

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Abstract

The giant Obuasi deposit, Ghana, is the largest gold mine discovered in West Africa with 62 Moz of gold. The deposit is hosted in the Birimian sedimentary rocks of the Kumasi Group, close to the contact with the Ashanti greenstone belt. Two economic styles of mineralization coexist, but were formed during different structural events. The first style consists of sulphide ore, mainly composed of gold-bearing arsenopyrite disseminated in the metasedimentary rocks, and formed during NW-SE shortening (D2\textsubscript{Ob}). The second style consists of high grade visible gold hosted in thick quartz veins up to 11 metres wide. The visible gold distribution is controlled by late fracturing and folding of the quartz veins during NNW-SSE to N-S shortening (D3\textsubscript{Ob}). While the arsenopyrite mineralization is characterized by an extensive ankerite-siderite alteration halo, the alteration footprint of the visible gold ore is only weakly marked by a late generation of chlorite porphyroblasts in the adjacent metasedimentary rocks. Three major styles of ore shoot have been identified: (1) volcanic unit and dyke controlled ore shoots, (2) fault intersection controlled ore shoots, and (3) F3\textsubscript{Ob} fold hinge controlled shoots.

1. Exploration history and introduction

Obuasi, or “under the rock” translated from the local Tchi language, is the largest gold deposit discovered in West Africa to date. Artisanal gold mining at Obuasi is ancient, with the local gold seekers, the Galamsey, panning and digging the quartz veins cropping out at the surface since before the 15\textsuperscript{th} century. Industrial mining officially started as far back as 1897 in the form of the newly established Ashanti Goldfields Corporation. 115 years later (2012) 32.5 Moz (921 t) of gold has been extracted mostly by underground mining but also from large open pits.

Underground and surface exploration estimates the resource at 29.8 Moz (844 t) of gold (2012). The exploration in the “Obuasi Deeps” is still active over 1500m deep and the lower extent of the deposit is yet to be reached.

The Obuasi deposit, extreme by its size, has been the focus of numerous studies (Junner, 1932; Wilson, 1972; Amanor, 1979; Gyapong, 1980; Bowell et al., 1990; Schwartz et al., 1992; Blenkinsop et al., 1994; Bowell, 1994; Höhndorf et al., 1994; Oberthür et al., 1994; Klemd et al., 1996; Mumm et al., 1997; Yao and Robb, 2000; Yao et al., 2001; Allibone et al., 2002; Fougerouse et al., in press). In this contribution, we present the latest understanding of the geology and mineralization at Obuasi.
2. Geological background

The Birimian rocks in Ghana consist of alternating volcanosedimentary rocks (Kumasi Group) and volcanic greenstone rocks (Sefwi Group; Adadey et al., 2009). The deposit is hosted in the carbonaceous phyllites, psammite, slate and intercalated volcanosedimentary rocks of the Kumasi Group close to the contact with the Ashanti greenstone belt (Figure 1). The sediments have been dated by U-Pb on detrital zircons to be younger than 2155 Ma (Oberthür et al., 1998). The Ashanti greenstone belt is composed of mafic volcanic and volcaniclastic rocks (Sefwi Group). The age of the extrusive volcanism of the Sefwi Group is given by U-Pb on zircon of a rhyolitic flow at 2189 ± 1 Ma (Hirdes and Davis, 1998). The belt is intruded by tonalite-granodiorite suites (the “belt type”), with a U-Pb zircon age of 2172 ± 2 Ma (Hirdes et al., 1992), which also provides a lower limit to the age of deposition of the mafic host rocks. A second generation of granitic to granodioritic rocks (the “basin type”) intrudes the Kumasi Group at 2105 Ma at Obuasi (U-Pb zircon; Oberthür et al., 1998). This later generation hosts gold mineralisation in the western Binsere trend (Figure 1; Anyankyerim, Nhyaso, Yaomensakrom).
Figure 1: Geology of the Obuasi district.
The rocks at Obuasi are strongly deformed and a multistage deformation history has been identified (Blenkinsop et al., 1994; Allibone et al., 2002; Fougerouse et al., in press). Based on new field data and the reassessment of previous data, Fougerouse et al. (in press) demonstrated that the structures and foliations define a three stage sequence, in which the subscript “Ob” refers to the structural framework at Obuasi identified by Fougerouse et al., (in press), while the subscripts “Al” and “Bl” indicate fabrics described by Allibone et al. (2002) and Blenkinsop et al. (1994; Figure 4).

The oldest fabric (S1 Ob) recorded is poorly preserved and has a small angle with respect to the bedding (S0). S1 Ob is folded and transposed by later structures and fabrics (Allibone et al., 2002).

The dominant foliation in Obuasi (S2 Ob), strikes northeast and dips steeply southeast to northwest, is axial planar to and formed coeval with F2 Ob folds. The F2 Ob isoclinal folds plunge dominantly northeast but variations include plunges to the southwest. The main S2 Ob cleavage is interpreted to be the result of a NW-SE directed shortening (D2 Ob). The major faults and shear zones in the district share the same orientation as S2 Ob and are interpreted to form during D2 Ob. The large quartz veins hosting the visible mineralisation also formed during D2 Ob (although the mineralisation developed at a later stage; see below). Subhorizontal stretching occurred during the late stage of D2 Ob with boudinage of quartz veins and granitic dykes and the formation of quartz pressure shadows around sulphides. This event represents a period where strain was accommodated by pervasive flattening and stretch, and localised high strain along shear zones (Fougerouse et al., in press). D2 Ob corresponds to D2 Al and D1 Bl.

These fabrics are overprinted by a crenulation cleavage (S3 Ob) and coeval generation of folds (F3 Ob). The intensity of S3 Ob varies across the Obuasi Mine, strikes east-northeast and dips shallowly to the north-northwest. F3 Ob plunges 20° to 50° to the northeast. D3 Ob corresponds to a NNW-SSE to N-S shortening direction and is similar to D4 Al and D2 Bl.

Allibone et al. (2002) reported a flat-lying (S3 Al) cleavage that trends northeast, as well as mineralized quartz veins that were interpreted to form during late sinistral strike-slip displacement on shear zones (late-D4 Al to D5 Al). The significance of these fabrics is discussed in more detail in Fougerouse et al. (in press) and they may reflect localised deformation rather than distinct regional tectonic events.

A muscovite, chlorite, actinolite and epidote mineral assemblage define greenschist facies metamorphism at Obuasi (Oberthür et al., 1994). Calculated P-T ranges, based on the stability of the mineral assemblage of actinolite + chlorite + clinozoisite + quartz + calcite implies conditions of 400 ± 50°C at 2 kbars (Schwartz et al., 1992). Peak metamorphic conditions occurred during D2 Ob of the Eburnean Orogeny.
3. Mineralization

3.1. Ore mineralogy

Mineralisation at Obuasi is classified into two types, (1) sulphide-hosted and (2) quartz vein hosted ores. Sulphide-hosted ore (1; Figure 2a) is dominated by arsenopyrite (60-95%) with lesser amounts of pyrite, pyrrhotite, marcasite, chalcopyrite, and rare micrograins of native gold (Oberthür et al., 1994). The larger arsenopyrite grains are zoned with gold-poor cores and gold-rich rims (Oberthür et al., 1994; Oberthür et al., 1997; Fisher et al., 2014). Gold is refractory and locked in the sulphide lattice (Oberthür et al., 1994). The abundance of arsenopyrite increases with the proximity of the graphitic shears.

Quartz vein ores (2; Figure 2c) are associated with spatially variable but exceptionally high grades of visible gold in thick quartz veins (up to 25 m). The visible gold is hosted in micro-fractures that overprint quartz veins (Fougerouse et al., in press). Commonly, the quartz veins border graphitic shears zones. Several thick quartz veins may be present in the same ore zone. The veins mainly comprise quartz but also minor amounts of ankerite and host rock fragments. Their mineralized microfractures contain muscovite, gold, graphite and accessory minerals such as galena, chalcopyrite, sphalerite, bournonite, boulangerite, tetrahedrite, aurostibine, löllingite, pyrite, arsenopyrite, and rare bismuth tellurides (Oberthür et al., 1994).
Figure 2: a) Microphotograph of the sulphide ores disseminated in phyllites. Gold-bearing arsenopyrites are surrounded by strain shadows parallel to S2Ob and refolded by S3Ob; b) Carbonate alteration halo in the wall rock (phyllites). The ankerite crystals are surrounded by strain shadows aligned with S2Ob and refolded by S3Ob; c) Visible gold mineralization in the fractures of the quartz veins; d) BSE image of the wall rock (phyllites). Chlorite alteration minerals overprint the S3Ob cleavage.
3.2. Ore body characteristics

The Obuasi deposit is confined to the Ashanti fault zone. The mineralized part of the Ashanti thrust fault extends for 8 km, is several hundred metres wide and is subdivided into highly mineralized splay faults, referred to as “fissures” in local parlance. Commonly, these faults consist of a succession of small graphitic shears. The mineralization is entirely contained between these graphitic shears. The major mineralized splays are the Obuasi, Ashanti, Côte d’Or, Insintsium, Lode 3 or Big Blow fissures. In this section the term volcanic rock refers to the mafic volcaniclastic rocks and felsic dykes (Sansu dyke) of the Kumasi Group.

Three groups of ore shoot are described on the basis of geometry with; 1) volcanic rock controlled shoots, 2) fault intersection and bifurcation, and 3) F3Ob fold hinge controlled shoots (Allibone et al., 2002; Fougerousse et al., in press). Figure 3 presents a long-section projection of high grade mineralization and lithologies along the Main Trend.

The first group of ore shoots has atypical geometries that correlate with the location of the metavolcanic rocks (Figure 3). The most remarkable example of this type of ore shoot is the Sansu ore body, cropping out at the surface in the Sansu pit. Exploration below the 50 level at more than 1500 m deep has not yet reached the base of this mineralisation.

The second group of ore shoots can be subhorizontal, plunge steeply to the northeast or shallow to the south. This ore shoot group corresponds to anastomosing fault splays, and areas where fault tip bifurcation lines enhance permeability and fluid circulation (e.g. Walsh et al., 1999). The largest ore shoot of this type is where the Ashanti Fissure and Obuasi Fissure merge (Adansi ore shoot; Figure 3).

The third and most dominant ore shoot group plunges moderately to the northeast at 20° to 40°. It corresponds to F3Ob fold hinges of the graphite-rich shear zones (Blenkinsop et al., 1994; Allibone et al., 2002; Fougerouse et al., in press). Examples of this type of ore shoot are Coral Snake and SVS (Figure 3).
Figure 3: Projected long-section of high-grade ore shoots, underground infrastructure. Steep and sub-horizontal ore shoots coincide with the intersection of faults. In contrast, moderately plunging ore shoots are associated with folding (F3ob) of graphitic-rich fault zones (modified from Allibone et al., 2002).
Numerous satellite deposits are hosted in two other mineralised trends located west and east of the Obuasi mine. These trends share the same trend as the Ashanti fault (Figure 1). The Binsere trend, located to the west, comprises granite-hosted deposits. The mineralization in the Binsere trend is confined to hydrothermally altered calc-alkaline granite bodies and the adjacent metasedimentary rocks (Anyankyerim, Kunka, Yaoensakrom and Nyhiaso). The eastern Gyabunsu trend hosts mineralization in carbonaceous phyllites adjacent to contacts with more competent greywackes or volcaniclastic rocks. The mineralization in the Gyabunsu trend is mainly composed of gold-bearing sulphides and rare visible gold in boudinaged quartz veins and breccias.

3.3. Timing of mineralization

The relative timing of mineralisation at Obuasi has been much debated (Blenkinsop et al., 1994; Oberthür et al., 1994; Allibone et al., 2002; Fougerouse et al., in press). Allibone et al. (2002) previously interpreted all the gold mineralization to be coeval with a late sinistral reactivation of the Ashanti fault system (late-D4Al to D5Al). Fougerouse et al. (in press) recently documented a multistage mineralization history (Figure 4). The first episode is characterised by gold-bearing arsenopyrites (sulphide ores) during D2Ob. The gold-bearing arsenopyrites parallel the S2Ob cleavage and have strain shadows parallel with S2Ob, and refolded by S3Ob. The second episode of mineralisation during D3Ob corresponds to visible gold overprinting the quartz veins formed earlier, during D2Ob (quartz vein ores). The highest gold grades and the visible gold mineralisation are specifically located in fractures in the hinges of the F3Ob folds, as documented by micron-scale high-resolution X-ray computed tomography of quartz samples, underground mapping and deposit-scale 3D visualisation (Fougerouse et al., in press).

Furthermore, considering the results of Allibone et al. (2002), a potential third minor mineralizing event, controlled by late sinistral strike-slip movements during late-D4Al to D5Ah, may exist in parts of the Obuasi deposit and is limited to a small amount of arsenopyrite grains and gold veining in localized areas of the Obuasi mine.

Although the two events defined by Fougerouse et al. (in press) are distinct, they both likely occurred during the Eburnean orogeny, with the early stage of mineralization constrained by U/Pb zircon ages of the Anyankyerem granite to younger than 2106 ± 2 Ma (Oberthür et al., 1998).

3.4. Alteration features

A 25-50 m ankerite-siderite alteration halo surrounds and precipitates contemporaneously with the arsenopyrite mineralisation (Fougerouse et al., in press). These carbonates (Figure
2b) share the same microstructural position as the arsenopyrites, with minerals aligned parallel with the S2Ob cleavage. They also have strain shadows crenulated by S3Ob.

In the metasedimentary rocks, in close proximity to the quartz veins that are mineralised by high grade visible gold, the S3Ob cleavage and matrix minerals (muscovite and quartz are overprinted by a weakly developed, late generation of chlorite porphyroblasts (figure 2d).

4. Summary

The Obuasi gold deposit is the largest discovered in the Birimian of West Africa to date. The deposit is hosted in the Kumasi volcanosedimentary basin close to the contact with the Ashanti greenstone belt. A complex deformation, mineralization and alteration history has been defined. Fougerouse et al., (in press) described a 3 stage structural sequence consisting of D1Ob (only weakly preserved and interpreted as a bedding parallel shearing), D2Ob the main NW-SE shortening event and D3Ob, a N-S to NW-SE shortening event. Two distinct styles of mineralization coexist, the sulphide ores (gold-bearing arsenopyrites disseminated in metasediments) and the quartz vein ores (native gold in quartz veins). The gold-rich arsenopyrite ores and large quartz veins precipitated during D2Ob, and are associated with an ankerite and siderite alteration halo. This relationship is typical for orogenic gold systems in sedimentary rocks (Eilu, 1999; Groves et al., 1998; Eilu and Groves, 2001).

The Obuasi system was then overprinted twice, first by an episode of sub-horizontal stretching in the last stage of D2Ob. This event created strain shadows around gold-bearing arsenopyrite and carbonate porphyroblasts, and also caused boudinage of the quartz veins (Figure 4).

The second overprint occurred during D3Ob and the refolding of the units. The mineralized graphitic shear zones were refolded during D3Ob. The dominant ore shoot group (Group 3) is related to F3Ob fold hinges of the graphite-rich shear zones, and therefore are interpreted to have formed during D3Ob (Figure 4). The quartz vein ores have been overprinted and folded during D3Ob. A late generation of arsenopyrites could have precipitated during this event (Allibone et al., 2002). The footprint of this visible gold mineralization event is characterized by a weakly developed chlorite alteration halo.
Figure 4: Structural and metallogenic evolution of the Obuasi deposit. The notation $30 \rightarrow 45$ indicate the average trend and plunge of the $F_3_{\text{Ob}}$ folds. Mineral abbreviation: Apy, arsenopyrite; Py, pyrite; Au, gold; Gn, galena; Ccp, chalcopyrite; Sp, sphalerite; Brn, bournonite; Ast, aurostibine.
Acknowledgements

The authors would like to acknowledge AngloGold Ashanti Ltd for their financial support and access to the mine site. The Obuasi geology team is acknowledged for sharing their experience, especially C. Asamoah-Owusu, W. Agongo, W. Kportufe and R. Kumi. C. McCuaig and J. Miller acknowledge receipt of a large ARC linkage LP110100667 grant. The authors acknowledge the facilities, and the scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy, Characterisation & Analysis, The University of Western Australia, a facility funded by the University, State and Commonwealth Governments. This is contribution 638 from the ARC Centre of Excellence for Core to Crust Fluid Systems (http://www.ecfs.mq.edu.au).

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Appendix III: 12th Biennial SGA Meeting

Appendix III:

Multistage mineralization of the giant Obuasi gold deposit, Ghana

Accepted for oral presentation at the 12th Biennial SGA Meeting, 12–15 August 2013, Uppsala, Sweden

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Abstract.

Debate surrounds many of the world’s largest gold deposits as to whether they benefited from multiple episodes of mineralization. The giant Obuasi gold deposit in western Africa is hosted in metasediments affected by a complex deformation history, with at least three structural stages. We used a combination of underground and field mapping, 3D visualization of drill core data, and microstructural studies to investigate the controls on gold mineralization. The majority of the resource is contained between graphite-rich shears, in two distinct styles. These include gold-bearing disseminated arsenopyrite in sedimentary rocks and visible gold within microfractures in quartz veins as much as 4-m-thick. Microstructural observations demonstrate that the arsenopyrite-hosted ore formed coevally with the second stage of cleavage development. In contrast, the underground/field mapping and the 3D visualization of drill core data indicate that the visible gold ore formed coevally with the latest stage of folding and cleavage development. Our results confirm that the Obuasi gold deposit formed during at least two different structural stages. This may indicate that gold was locally remobilized from arsenopyrite into late-stage microfractures, or it may be due to two overprinting and unrelated mineralizing events.

Keywords. Ghana, gold, multistage, Birimian, Ashanti
Appendix III: 12th Biennial SGA Meeting

1 Introduction

The giant Obuasi gold deposit (also named the Ashanti mine) is the largest deposit in western Africa, with more than 60 Moz of gold. The deposit extends for 8 km along strike and is 1.6-km-deep, with active exploration continuing below this depth. The deposit is located at the contact between the Kumasi volcanosedimentary basin and the Ashanti greenstone belt. It contains more than 20 individual ore shoots within a corridor between graphite-rich fault planes belonging to the Ashanti fault.

There are two distinct gold mineralization styles;

1. sub-microscopic gold contained within arsenopyrite and, less commonly, in pyrite,
2. visible gold contained within micro-factures, hosted in quartz veins as much as 4-m-thick, which border the graphite-rich fault rock.

Two competing models have been invoked to explain mineralisation at Obuasi. Oberthür et al. (1994) argued that the sulfide ores predate the quartz veins ores, but did not distinguish whether there were two distinct mineralization events or two different styles that overlapped in time. Conversely, Allibone et al. (2002) concluded mineralization occurred at a late stage during sinistral reactivation of the Obuasi shear zone during NW-SE to N-S shortening. The present study re-examines the timing of mineralization at Obuasi and tests between these two existing models, using new data made available due to development of the mine.

2 Geological setting

The Paleoproterozoic Birimian belts in Ghana consist of volcanosedimentary basins and volcanic greenstone belts (Fig. 1), intruded by several generations of granitoids (Junner 1935; Leube and Hirdes 1986; Leube et al. 1990). The Birimian belts were formed during the Eburnean orogeny between 2200 and 2088 Ma (Bonhomme 1962; Abouchami et al. 1990; Allibone et al. 2002). The volcanic belts are older than 2186 Ma based upon U/Pb zircon ages obtained from intruded granitoids (Boher et al. 1992; Hirdes et al. 1992; Oberthür et al. 1998), but the sedimentary rocks of the basins are younger than 2130 Ma based upon U/Pb on detrital zircons (Davis et al. 1994; Oberthür et al. 1998). The conglomeratic Tarkwaian rocks are the product of inversion and erosion of the previously formed volcano-sedimentary basins. The eroded rocks were then deposited as conglomerates over the greenstone belts (Allibone et al. 2002). Gold mineralization is thought to be temporally associated with the post-metamorphic peak of the Eburnean orogeny, at ca, 2100 Ma (Milesi et al. 1989).
The Obuasi gold deposit is hosted in the Kumasi volcano-sedimentary basin, within turbiditic and volcanoclastic sedimentary rock. All gold mineralization at Obuasi is either spatially associated with or hosted within the Ashanti fault (Blenkinsop et al. 1994; Oberthür et al. 1994; Allibone et al. 2002).

A complex structural sequence has been recognized at Obuasi, and two slightly different schemes have been previously proposed to explain this (Blenkinsop et al. 1994; Allibone et al. 2002). There is an early cleavage (S1) that is only weakly developed and has an acute angle with respect to the bedding (S0). The second and most dominant cleavage (S2) strikes northeast and dips steeply to the northwest. The F2 fold axes gently plunge to the northeast. Peak metamorphic conditions occurred at 400±50°C and 2 kbar (Schwartz et al. 1992) during the development of this S2 cleavage. Finally, late cleavage (S3) and associated fold axial planes strike east-northeast, with gentle to steep dips to the north-northwest. The F3 folds deform previous structures. The fold amplitudes are centimeter to tens of meter in scale, with axes plunging at 20 to 50° to the northeast.

It has been proposed that the northeast-striking graphitic faults hosting the mineralization may have nucleated along early S1 cleavage (Allibone et al. 2002). The second and main S2 cleavage is the results of a NW-SE compression (D2) that transposed S0 into S2 cleavage. This fabric is S1 in the structural sequence defined by Blenkinsop et al., (1994). The late S3 cleavage is interpreted to be the product of a NNW-SSE to N-S shortening. This fabric is referred to as S2 and S4 by Blenkinsop et al. (1994) and Allibone et al. (2002), respectively.
Figure 1. Geological map of Northern Ghana geology and locations of major gold deposits (modified from Allibone et al., 2002).
3 Ore types and geometry

3.1 Disseminated sulfide ores

Greater than 50% of the gold production in Obuasi is derived from gold-bearing sulfides which are disseminated in metasedimentary rock (Milési et al. 1991). The textures, timing, geological setting, and chemistry of this ore have been previously examined by Leube et al. (1990) and Oberthür et al. (1994). The ore mineralogy comprises arsenopyrite, pyrite, pyrrhotite, marcasite, chalcopyrite, and rare micrograins of native gold (Oberthür et al. 1994). The ore mineral are dominated by arsenopyrite (60-95%). Several generations of arsenopyrite exist, with zonation present in the bigger crystals. Within the arsenopyrite, gold is heterogeneously distributed as gold-rich rims and gold-poor cores (Oberthür et al. 1994). Gold is also locked in the crystal lattice of sulfides, as micronuggets close to arsenopyrite or in microfractures cutting arsenopyrites.

Strain shadows are present in association with a large proportion of the gold-bearing arsenopyrite and pyrite. The strain shadows are developed along the S2 cleavage and are microfolded by the S3 crenulation cleavage (Fig. 2).

However, some arsenopyrites do not display any strain shadows, indicating that there may be multiple generations of arsenopyrite nucleation and growth. Allibone et al. (2002) present possible evidence for needles of arsenopyrite overprinting the latest cleavage (S3 this study).
Figure 2. Optical microphotograph, and interpreted sketches; Quartz strain fringes developed along S2 and folded along S3; sample DF038, Obuasi underground (L21 XC343).
3.2 Quartz vein ores

The highest grade ores at Obuasi are contained within thick quartz veins, as much as 4-m-wide. These ores are characterized by visible gold in microfractures cutting through, but contained entirely within the quartz veins. The quartz veins usually dip to the west and are very close to the graphitic shears. Several quartz veins may be present in the same ore zone. The veins comprise quartz, minor ankerite, and host rock fragments. The quartz can have a smoky, milky, or glassy appearance, but only the first two categories are associated with elevated gold grades. Within the microfractures, gold is accompanied by muscovite, graphite, galena, chalcopyrite, sphalerite, bourronite, boulangerite, and aurostibine (Oberthür et al. 1994).

3.3 Deposit-scale geometry

At the kilometer-scale, in long-section, both ore types are associated with two distinct geometric styles, which can be related to at least two separate structural controls (Fig. 3). The first style of ore shoot is steeply dipping to the northwest, or subhorizontal in long-section, and this corresponds to branch-lines derived from fault splays (Walsh et al. 1999). The second style plunges moderately (30-50°) to the northwest, corresponding to F3 folding of the Ashanti fault and the intersection line between the Ashanti fault and S3 cleavage (Blenkinsop et al. 1994).
Figure 3. Projected long-section of high-grade ore shoots, underground infrastructures, and surface mining. Steep and horizontal ore shoots coincide with the intersection of fault splays. In contrast, moderately plunging ore shoots are associated with both folding of the Ashanti fault system (F3) and/or the intersection of S3 cleavage (modified from Allibone et al. (2002)).
4 Discussion

Recent studies compiling craton-scale observations have highlighted how several stages of mineralization can be identified in the larger gold deposits of well-endowed greenstone terrains, such as in the Superior and Yilgarn cratons (Robert et al. 2005).

At the Obuasi deposit, two models exist for the timing of gold mineralization (Oberthür et al. 1994; Allibone et al. 2002). The first model states that the sulfide ore predates the quartz vein ore based on evidence from ore mineralogy and textures (Oberthür et al. 1994). Oberthür et al. (1994) argued that the two ore styles may have formed progressively during transition from a regime dominated by ductile deformation processes and pervasive fluid flow to a brittle regime. The second model is that a late sinistral reactivation of the fault system controls the gold mineralization. This model is based upon the field mapping of dilatational jogs matching the ore shoot position, as well as vein asymmetries showing sinistral motion during their formation (Allibone et al. 2002).

Relative to the structural sequence defined in this study, we find that the gold-bearing arsenopyrite grains formed pre- to syn-D2, based on the geometry and deformation of their strain shadows (Fig. 2). This constitutes an early stage of mineralization within the Obuasi system.

In contrast, the geometry of the ore shoots, containing high grade ore and visible gold mineralization, are parallel with F3 folding of the Ashanti fault and/or the intersection of the fault with the S3 cleavage. This geometric relationship implies microfracturing of quartz veins and precipitation of visible gold occurred during D3. In addition, the vein style ore is associated with a different mineral assemblage relative to the disseminated ore.

In summary, the results of this study indicate the Paleoproterozoic Birimian terranes of western Africa host large deposits, which underwent multiple episodes of gold deposition. The giant Obuasi gold deposit has been subjected to at least two episodes of mineralization. It is not yet clear whether the vein ores are the product of remobilization of gold from the disseminated ores, or whether the two ore types are genetically unrelated, but spatially overlapping. Research is ongoing to constrain the timing and origin of the different mineralization episodes observed at the Obuasi gold deposit.
**Acknowledgements**

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Appendix IV:

Is gold an immigrant or a neighbour – remobilization in the giant Obuasi gold deposit, Ghana?

Accepted for poster presentation at the SEG 2014: September 27-30, 2014, Keystone, CO, USA.

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Appendix IV: SEG 2014

Abstract

Many of the world’s largest gold deposits contain evidence of multiple mineralizing events. Whether or not gold is remobilized or derived from separate, overprinting hydrothermal systems is a matter of some controversy. The 60 Moz Obuasi deposit, Ghana, has two contrasting styles of mineralization with 50% of the resource contained in disseminated arsenopyrites in sedimentary rocks and 50% as high-grade native gold, occupying fracture networks in previously deformed quartz veins. We constrained the microstructural and microchemical evolution of the arsenopyrite ore during metamorphism and deformation, using a combination of Scanning Electron Microscopy (SEM), Electron Backscattered Diffraction (EBSD), Secondary Ion Mass Spectrometer (SIMS), and quantitative synchrotron X-ray Fluorescence Microscopy trace element mapping with the Maia large solid-angle detector array at the Australian Synchrotron. EBSD reveals gold-bearing arsenopyrites deformed via crystal-plasticity, which led to the development of subgrain boundaries and a small number of new grains. The recrystallized areas became focal points for subsequent brittle microfracturing. In these deformed regions, gold concentrations are significantly lower and selected grain boundaries of the arsenopyrites have undergone significant dissolution. Coeval with the microfracturing and dissolution, a generation of pyrites precipitated with native gold inclusions. The results indicate that significant quantities of gold were remobilized from gold-rich growth zones within arsenopyrite and potentially reconcentrated at much higher grades within the fracture networks in adjacent quartz veins. Crystal-plasticity, microfracturing, dissolution and nanoscale dissolution-reprecipitation replacement reactions were likely all important mechanisms in releasing gold from the arsenopyrite crystal lattice. Field relationships and petrography reveal that low-strain deformation and incipient recrystallization of arsenopyrite as well as embrittlement and gold remobilization occurred during late folding of the host rocks postdating the main phase of arsenopyrite crystallization.
Appendix V:

Two stages of mineralization due to remobilization: Obuasi gold deposit, Ghana

Accepted for poster presentation at the Gold14@Kalgoorlie international Symposium, 8-10 October 2014, Kalgoorlie, Australia.

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Abstract

Many of the world’s largest gold deposits contain evidence of multiple mineralizing events. Whether or not gold is remobilized or derived from separate, overprinting hydrothermal systems is a matter of some controversy. The 60 Moz Obuasi deposit, Ghana, has two contrasting styles of mineralization with 50% of the resource contained in disseminated arsenopyrites in sedimentary rocks and 50% as high-grade native gold, occupying microfracture networks in deformed quartz veins (Junner 1932; Schwartz et al. 1992; Blenkinsop et al. 1994; Oberthür et al. 1994; Allibone et al. 2002; Fougerouse et al. 2013). We combined underground and field mapping and 3D visualization of the large drill core database with microstructural studies, to investigate the controls on gold mineralization. We constrained the microstructural and microchemical evolution of the arsenopyrite ore during metamorphism and deformation, using a combination of Scanning Electron Microscopy (SEM; fig. 1A), Electron Backscattered Diffraction (EBSD; fig. 1B), Secondary Ion Mass Spectrometer (SIMS; fig. 1C), and quantitative synchrotron X-ray Fluorescence Microscopy trace element mapping with the Maia large solid-angle detector array at the Australian Synchrotron.

Petrographic observations demonstrate that the arsenopyrite-hosted ore formed relatively early, during the main cleavage development, but that the visible gold occupies microfractures postdating this event. Detailed underground mapping and the 3D modelling of gold grade from the drill core data indicate that the visible gold ore formed coevally with a late stage of folding and crenulations cleavage development. At the microstructural level, EBSD reveals gold-bearing arsenopyrites were deformed via crystal-plasticity, which led to the development of subgrain boundaries and the production of a small number of new grains. The recrystallised areas became focal points for subsequent brittle microfracturing. Mapping of chemical zonations using SIMS and the Maia detector shows that, in these deformed regions, gold concentrations are significantly lower, whereas nickel concentrations are increased by a factor of 5. Furthermore, elevated nickel is contained in pyrites associated with visible gold adjacent to the grain boundaries of the arsenopyrites that have undergone significant dissolution.

We conclude that significant quantities of gold were remobilized from gold-rich growth zones within arsenopyrite and reconcentrated at much higher grades within the microfracture networks in adjacent quartz veins. Low-strain crystal-plasticity, microfracturing, dissolution and nanoscale dissolution-reprecipitation replacement reactions were likely all important mechanisms in releasing gold from the arsenopyrite crystal lattice. Gold remobilization occurred during late folding of the host rocks, postdating the main phase of arsenopyrite
crystallization (fig. 1D). We demonstrated here that Obuasi underwent at least two stages of mineralization with the last stage resulting in a significant upgrade of the resource.

Figure 1. A) backscattered image of a gold-bearing arsenopyrite; B) crystal lattice orientation (EBSD) of the grain, coloured according to misorientation. Deformation formed subgrains and new grains; C) SIMS gold distribution, the grain is zoned with gold-poor core and gold-rich rim. Zones 3 are depleted in comparison to zones 2; D) Interpretation of the crystallization and deformation of the arsenopyrite.
References

Appendix VI:

Gold remobilisation from Arsenopyrite: Crystal-plasticity and dissolution-reprecipitation reactions

Accepted for poster presentation at the 13th Biennial SGA Meeting, 24–27 August 2015, Nancy, France.

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Appendix VI: 13th Biennial SGA Meeting
Abstract

The significance of gold remobilisation in ore deposits is a contentious issue. The microstructural and geochemical evolutions of arsenopyrite ores from the 62 Moz Obuasi deposit, Ghana, reveal the mechanisms for how such a process may operate. The arsenopyrite ores were coeval with high strain deformation and metamorphism in the country rocks (400±50°C and 2 kbar). The majority of the arsenopyrite crystals are zoned with a gold-poor core and epitaxial rims (A-rims). The epitaxial rims are characterised by oscillatory zoning and high concentrations of gold (up to 1000 ppm) in the crystal lattice. Commonly, cores and A-rims are dissected by gold-depleted zones (B-rims) associated with microfractures, grain boundaries and subgrain boundaries formed during recrystallisation. B-rims are interpreted as alteration zones with sharp reaction fronts, which formed post-peak metamorphism and deformation. We develop a model whereby grain-scale microfractures and crystal-plastic microstructures facilitate a dissolution-reprecipitation replacement reaction and the release of gold from the arsenopyrite crystal lattice. At Obuasi, this gold appears to have contributed to a significant upgrade in the form of ultra-high grade ore shoots with visible gold.

Keywords. Remobilisation, multistage mineralisation, gold, arsenopyrite, replacement, crystal plasticity

1 Introduction

Gold-bearing sulphides are a common feature of orogenic gold deposits forming large, low grade disseminated mineralisation (Groves et al. 1998). Gold remobilisation from these sulphides during metamorphism is potentially of critical importance to resource upgrading or downgrading and then mineral exploration.

Two main processes have been proposed to explain trace element remobilisation; 1) hydrothermal fluid interacting with the sulphide (solid-fluid state; Putnis et al., 2009 and references therein) and 2) intragrain diffusion (solid-solid state; Vukmanovic et al., 2014 and references therein). Hybrid models have been documented where solid-solid diffusion is mediated by a fluid phase (Plümper et al. 2012).

In this study we focused our attention on the well documented Obuasi gold deposit (Ghana), where gold-bearing arsenopyrite mineralisation in metasedimentary rocks is adjacent to visible gold mineralisation in quartz veins (Oberthur et al. 1994; Allibone et al.
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2002; Fougerouse et al. in press). We used a combination of high resolution Secondary Ion Mass Spectrometry (NanoSIMS), Electron backscattered diffraction (EBSD) and Scanning Electron Microscopy (SEM) to analyse gold-bearing arsenopyrites previously well constrained by field mapping and 3D modelling (Fougerouse et al., in press). We apply this approach to identify the mechanisms that contribute to the loss of gold from arsenopyrites.

2 Deformation history and relative gold timing

A complex deformation, mineralisation and alteration history has been defined at Obuasi (Fougerouse et al. in press; Allibone et al. 2002; Oberthür et al. 1994; Blenkinsop et al. 1994), and recently updated by Fougerouse et al. (in press). There are two co-located economic styles of mineralisation formed during distinct events (Fig. 1). Firstly, arsenopyrite-hosted ore formed during the main NW-SE shortening direction event (D2Ob). Subsequently, high grade visible gold mineralisation was controlled by later fracturing and folding of quartz veins during NNW-SSE to N-S shortening (D3Ob). This sequence was defined using field observations from underground and deposit scales, and high-resolution X-ray computed tomography that revealed gold distributed in fracture networks overprinting the quartz veins (Fougerouse et al., in press).

<table>
<thead>
<tr>
<th>DEFORMATION</th>
<th>REPRESENTATIVE STRUCTURES</th>
<th>MINERALIZATION</th>
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<tr>
<td>D1&lt;sub&gt;Ob&lt;/sub&gt;</td>
<td>S1 rarely preserved bedding parallel shearing Similar to D1&lt;sub&gt;Al&lt;/sub&gt;</td>
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<td>D2&lt;sub&gt;Ob&lt;/sub&gt;</td>
<td>NW-SE shortening Steeply dipping NE striking S2&lt;sub&gt;Ob&lt;/sub&gt; F2&lt;sub&gt;Ob&lt;/sub&gt; tight to isoclinal folding, Large quartz veins, Sub-horizontal stretching (boudinage, BN=boudin neck) Similar to D1&lt;sub&gt;Al&lt;/sub&gt; and D2&lt;sub&gt;Al&lt;/sub&gt;</td>
<td>F2&lt;sub&gt;Ob&lt;/sub&gt;, BN</td>
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<td>D3&lt;sub&gt;Ob&lt;/sub&gt;</td>
<td>NNW-SSE shortening Gently dipping E to NE S3&lt;sub&gt;Ob&lt;/sub&gt; Asymmetric F3 folds F3&lt;sub&gt;Ob&lt;/sub&gt; = 30 → 45 Folding of the Ashanti fault Similar to D2&lt;sub&gt;Al&lt;/sub&gt; and D4&lt;sub&gt;Al&lt;/sub&gt;</td>
<td>S3&lt;sub&gt;Ob&lt;/sub&gt;, F3&lt;sub&gt;Ob&lt;/sub&gt;</td>
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Figure 1. Structural evolution and timing of mineralisation of the Obuasi deposit (Fougerouse et al. in press)
3 Crystal plastic deformation and trace element modification

3.1 Crystal zonation

Arsenopyrites from the ore zone of the Obuasi deposit are typically composed of two primary domains: a rim that appears homogenous in BSEM images (A-rim) and an inclusion-rich internal core (Oberthür et al. 1994; Oberthür et al. 1997). The core is usually gold poor (Oberthür et al. 1997) with inclusions of pyrrhotite, chalcopyrite or rutile. The homogenous A-rims represent epitaxial zones with up to 1000 ppm Au (Oberthür et al. 1994; Fisher et al. 2014).

Commonly, there is a third domain (B-rim) crosscutting all others (Fig. 2). B-rims are characterised by a higher than average atomic mass (lighter colour in BSE images due to higher As concentrations) and preserve the original shape of the crystals. The contacts between the B-rims and other domains in the arsenopyrites are sharp, planar to curvilinear (bulbous) and penetrate in microcracks and grain boundaries (Fig. 2). Visible gold particles can be observed in the microfractures that are associated with the B-rims.

3.2 Crystal plastic deformation

EBSD and NanoSIMS analyses were conducted on sample 215-20, to identify the processes affecting mineralised arsenopyrites, given the good field constraints on mineralised arsenopyrite and later visible gold. The grain shown in Figures 3-4 was selected on the basis of its large size (up to 1 mm) and homogeneity. The arsenopyrite is located parallel to the main cleavage (S2Ob) and at a high angle to a microfold of crenulation cleavage (S3Ob).

The EBSD data show a relative change in crystallographic orientation from a central point to a maximum of 10°, for each grain (Fig. 3). Consistent with other studies (Reddy and Hough 2013), we define high angle grain boundaries to have misorientations ≥10°. All boundaries <10° are low angle grain boundaries and define subgrains. In most cases the intragrain variation does not reach 5°, though new grains are formed at a few localised points. These observations are consistent with dynamic recrystallisation by dislocation creep. The spread of crystallographic orientations in pole figures of the grain indicate deformation occurred at a high angle to the long axis of the arsenopyrite crystal, suggesting that the crystal plasticity occurred during D3Ob.

Subgrains and rare new grains accommodate strain in a narrow localised domain on the top right-hand side of the crystal, coincident with a large microfracture (Fig. 3). This suggests the arsenopyrite underwent strain hardening during crystal-plastic deformation, eventually leading to embrittlement.
Figure 2. Backscattered images of arsenopyrite. Replacement rims (B-rims) cut across the primary zonation (A-rims). Top image: sample 215-7; bottom image: sample 318-15
Figure 3. Electron backscatter diffraction (EBSD) orientation map of arsenopyrite (sample 215-20), colored to show a relative change in crystallographic orientation up to 10°. The grain is deformed with strain localisation forming subgrains and dynamic recrystallisation producing new grains.
3.3 Trace element distribution

NanoSIMS analysis reveals that, within the A-rims, gold is distributed in alternating, micron- to submicron-scale concentric bands (Fig. 4), which are approximately parallel with the euhedral outline of the overall arsenopyrite grain. Up to 100 bands are present within the A-rims despite the rims homogenous appearance under BSEM. The fine resolution, oscillatory nature of these bands is much greater than previously detected using older, lower resolution techniques (Oberthür et al. 1994). These textures are interpreted to represent gold entrapment in the crystal lattice of arsenopyrite during epitaxial overgrowth.

The primary oscillatory zonation of the gold-rich A-rims is cut by B-rims characterised by high Ni and gold concentrations below detection level. The B-rims are discontinuously developed along grain boundaries and some microfractures. B-rims are not present along all microfractures suggesting different generations of fractures are present in the arsenopyrite grains. The Ni distribution also appears to be zoned in the B-rims, controlled by the crystallographic lattice, but in a manner that does not reflect the same lattice orientation as the oscillatory zoned gold (data not shown).
Figure 4. a) Backscattered image of an arsenopyrite; b) NanoSIMS image of the Ni distribution in the area indicated in (a). The pyrite in the healed microfracture as well as part of the replacement rims (B-rims) are nickel-rich; c) the gold distribution is finely zoned in the epitaxial growth bands. B-rims are deprived in gold; d) composite image, gold is yellow and nickel is blue. The grain and B-rims boundaries are highlighted in red.
4 Interpretation and Discussion

In summary, in the example presented, B-rims cut across the primary gold zonation of the arsenopyrites. Although these rims have a different composition (enriched in As and Ni), they preserve the original shape of the parent arsenopyrite crystal but have lost all detectable gold. The transition from A- to B-rims is sharp and the morphological characteristics of the B-rims are planar to curvilinear. These relationships are consistent with gold remobilization being controlled by a pseudomorphic dissolution-reprecipitation reaction (Putnis 2009; Harlov et al. 2005; Corfu et al. 2003; Geisler et al. 2007).

Furthermore, the EBSD data indicate that during the development of the S3Ob cleavage, at a high angle to the arsenopyrite long axis, small amounts of crystal plasticity generated subgrains and new grains in localized domains of the arsenopyrite. Gold-poor B-rim replacement zones penetrate further in the grain in these recrystallised zones. Taken together, the association between crystal plastic microstructure and larger replacement zones strongly suggests that the recrystallisation of the arsenopyrite and the formation of subgrains influenced the replacement reaction.

We conclude gold was extracted from the crystal lattice of the arsenopyrite and released into a low volume, grain-scale fluid phase during dissolution-reprecipitation replacement. This process was facilitated by domains of crystal-plastic microstructure (Fig. 5), most likely due to enhanced diffusion pathways for trace elements to and from the reaction front, along high and low angle crystallographic boundaries (e.g. Vukmanovic et al. 2014; Plümper et al. 2012). Plümper et al. (2012) proposed that the reaction can be enhanced by solid-state diffusion along subgrain boundaries. Subsequent transport distances of the gold, outside the arsenopyrite, were on the scale of millimetres to metres. High concentrations of visible gold then precipitated in microfractures within quartz veins, to form Obuasi’s super-high grade ore shoots.

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Figure 5. Interpretative diagram through time of crystallisation and deformation of the arsenopyrite.
Appendix VI: 13th Biennial SGA Meeting

References


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Appendix VII:

Gold remobilization in the Giant Obuasi deposit

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Abstract

The significance of gold remobilization in ore deposits is a contentious issue, largely because we poorly understand the mechanisms for how gold may be extracted from minerals then re-concentrated over short distances. The microstructural and microchemical evolution of arsenopyrite ores from the 62 Moz sediment hosted Obuasi deposit, Ghana, reveal the mechanisms for how such a process may operate. Two co-located economic styles of mineralization occur with gold trapped in the crystal lattice of arsenopyrite and as visible gold in fracture networks. To understand the metallogenical processes involved in the formation of these ores, we used a combination of field work, Scanning Electron Microscopy (SEM), Electron Backscattered Diffraction (EBSD), High-resolution X-ray computed tomography, Secondary Ion probes (SIMS and NanoSIMS) and quantitative synchrotron X-ray Fluorescence Microscopy trace element mapping at the Australian Synchrotron.

The arsenopyrite-hosted ore formed first during the main NW-SE shortening direction event (D2ob) while high grade visible gold mineralisation was controlled by later fracturing and folding of quartz veins during NNW-SSE to N-S shortening (D3ob). In the arsenopyrite ores the majority of the arsenopyrite crystals are zoned with a gold-poor core and epitaxial rims. The rims are characterized by a micron scale oscillatory zoning and high concentrations of gold (up to 1000 ppm) in the crystal lattice. Commonly, cores and rims are dissected by gold-depleted zones (B-zones) associated with microfractures, grain boundaries and subgrain boundaries formed during recrystallisation. B-zones are interpreted as alteration zones with sharp reaction fronts, which formed post-peak metamorphism and deformation during D3ob. We develop a model whereby grain-scale microfractures and crystal-plastic microstructures facilitate a dissolution-reprecipitation replacement reaction and the release of gold from the arsenopyrite crystal lattice. At Obuasi, this gold appears to have contributed to a significant upgrade in the form of ultra-high grade ore shoots with visible gold.