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Abstract
Using polarizing microscope, the Scanning Electron Microscope (SEM) and the LINKAM THM 600 techniques, genetic connections between opening of space, the filling with mobile hydrothermal fluid phase, of banded gold quartz veins from the Birimian rocks were studied. The internal structure and the filling along the vein-wall contact suggest a crack-seal mechanism of emplacement. Observations of inhomogeneous extinction of bands under crossed polars, show the opening direction across the vein. The ion content of the fluid inclusion that find their way into the interstice are controlled by low frequency and temperature. Microthermometric data on primary inclusions indicate that there are two main types of fluids: partly aqueous (CO₂-rich) fluid, and aqueous (H₂O-rich.) fluid. The limited range of the degree of fill (0.5 to 0.7) for the CO₂ – rich and H₂O – rich inclusions indicates the original homogeneous fluid. The CO₂-rich fluids homogenize at a higher temperatures (350 – 400°C) than the H₂O-rich fluids (310 – 370°C) and had salinity ≈5 wt % NaCl equiv. while H₂O-rich fluid had salinity ≈16 wt % equiv. Dominant trace gases in both fluids are CH₄ and N₂. Observations suggest that the geometric peculiarities of macroscopic growth mechanism may account for capillary effects. Based on this consideration, a simple quantitative model of quartz vein formation is proposed. This model provides a possible origin for the enhancement and maintenance of a diffusional mass transfer from the matrix to the position of the crack. The study of the development of such veins and dikes with discontinuities, is a vital tool to the discovery of hydrothermal gold and other economic minerals. It can also helps to understand crystal growth in localized weak planes within massive blocks of quartz, which in time and space may preferentially accommodate further brittle deformation; a phenomena which often affects long term sustainability of engineering projects such as hydro-dams and tunnels.

Keywords: hydrothermal gold, emplacement, fluid inclusions, quartz vein, birimian, microstructure.

INTRODUCTION
During the period 2,100 to 1,950 Ma (Cahen et al., 1984), the Paleoproterozoic rocks of the West African craton were deformed regionally, metamorphosed and tectonically stabilized. This period of time referred to as the Eburnean tectonic event is widespread over the African continent. In West Africa, it is recognized by the presence of linear zones of compressional sedimentary basins and tensional volcanic belts which are intruded by syntectonic and late-tectonic suites of granitoids. These north and northeastern striking belts of the sedimentary-volcanic rocks referred to as the Birimian is exposed in Ghana, Burkina Faso and Ivory Coast.

The economic mineral deposits in the Birimian in Ghana are gold and manganese. On the basis of structural and lithological belts, Mensah et al., (1988) divided Ghana into eight gold belts which represent geographic regions which are underlain by rocks with significant gold mineralization. Gold in the consolidated Birimian rock type occurs as massive auriferous sulphides in the wall rocks, particularly tuffaceous bodies termed as disseminated sulphide ore and quartz veins.

Generally, the quartz veins vary in width from 2 to 5 meters but sometimes can be up to 25 meters thick and the length may be 500 meters. The breath may vary with maximum figures of approximately 2 km. It is an established fact that hydrothermal gold transportation and deposition take place in a fluid phase and to have some knowledge of the gold transport and depositional conditions, fluid inclusion studies has to be carried out. Fluid inclusion studies usually involve thermometric and chemical studies on the fluids (i.e. liquids, gases and “frozen” melts) in the host mineral, which is quartz. These trapped fluids are assumed to have produced the various minerals in the quartz veins. Detailed past work on fluid inclusions has been focused on Ashanti mine (Schwartz et al., 1992, Oberthür et al., 1991). Though this illustrates controls on the auriferous fluid, lack of broad information at other mines or prospects (in similar geological environment as the
Ashanti Mine) may even lead to wrong identification of fundamental constraints on the auriferous fluids at Ashanti Mine. To help set up the basic fundamentals of the auriferous fluids in the Birimian, gold-bearing quartz veins were investigated from gold mines in different geological settings in the Birimian (i.e. in the metasediments, metavolcanics and in the metasediments/metavolcanics contact). Samples were taken from abandoned mines at various depths in the existing mines at Obuasi and Prestea (Fig. 2).

**GEOLOGICAL SETTING AND MATERIAL**

**Geology**

The Birimian rocks form a substantial part of the Man shield which occupies roughly the southern part of the West African craton (Fig. 1). The latter has remained stable since 1.7 Ga (Leube and Hirdes, 1986) and it is bounded to the north, east, and south by Pan African belts (Taylor et al., 1992). The Man shield comprises a western domain consisting essentially of Archaean rocks of Liberian age (3.0–2.5 Ga) and an eastern domain consisting predominantly of Birimian rocks of Paleoproterozoic age which were affected by a major tectonothermal event; the Eburnean event of around 2.15 Ga (Loh et al., 1999). This event led to shearing, folding, the mobilization of quartz fluid and the emplacement of banded quartz veins (Hayford, 1998) and the intrusion of granitoids (Bessoles, 1977; Hayford, 1998; Loh et al., 1999; Lompo, 2009).

Southern Ghana is covered principally by the Paleoproterozoic Birimian rocks. The prominent feature of the Birimian Supergroup of Ghana, is the existence of five parallel volcanic belts, several hundred kilometers in length. These consist of metabasalt, metadolerite metahyolites, quartzites and greywack and are separated by basins containing metasedimentary rocks made up of arenaceous and argillaceous subseries comprising: metasandstones metagreywacke phyllites and tufaceous varieties, and granitoids (Loh et al., 1999). Overlying the Birimian, is the Tarkwaian – a sequence of coarse clastic sedimentary rocks made up of conglomerates, sandstones, arkose, some subordinates of argillites and quartz veins.

**MATERIAL**

In the area of investigation (Prestea, Bogoso and Obuasi are different types, sizes, shapes and colours of quartz veins. This study however focuses on the banded quartz veins. The banded veins are mainly semi horizontal or semi vertical in orientation and are partly deformed (Fig. 3a,b).
The mobilize quartz veins found in a pegmatite (3a), shows discontinuities which is also the area of weaknesses within the vein. Observation shows, that crystals are coarse on the rim compared to that at the center. In Fig. 3b, crystal width reduces at the top and tail end of the vein indicating differentiation in the factors controlling the mobilization (from Hayford et al., 2009).

**METHODOLOGY**

Oriented quartz veins from target rocks (Fig. 3a, b)) were sampled. The selected samples were cut in directions normal to the regional foliation (N 60° E). The microstructures in thin sections (30µm thick) were examined using a polarizing microscope.

The areas in Fig. 4a where the width narrows up shows the points of discontinuity and structural weakness. Fig. 4b shows random mobilization of quartz as evidence, that mobilization takes place in areas where conditions of least resistance prevail. Fig.4a shows inhomogeneous extinction of bands under crossed polars indicating the opening direction across the band (from Hayford et al., 2009)

For the micro thermometric studies, using the LINKAM THM 600, samples were cut as wafers and polished using silicon carbide and MgO respectively to thickness of 2 to 3mm for fluid inclusion studies. For the sake of finding those inclusions which most likely represent the fluid which deposited the gold found in the quartz mineral, only the primarily inclusions were chosen for the micro-thermometric studies (Fig. 4a, b). Primary and pseudo-secondary inclusions which showed evidence of necking or leaking were rejected. Measurements were carried out on the LINKAM THM 600 stage with temperature range from -196 to +600 °C.
Fig. 5a, b shows fluid inclusion as function of the mobilization (from Hayford et al., 2009).

RESULTS AND OBSERVATION

Field observations show that the quartz veins are characterized by small lenses of veinlets irregularly formed and arranged parallel to the foliation of the host sedimentary and volcanic rocks (Fig. 3a). Microtexture of these quartz veins show that the crystals have varying sizes. The outer veinlets have larger crystal sizes compared to those in the core. Indeed the further away one moves from the core, the finer the crystals. The veins in the core are compact but cellular, porous and brecciated toward the rim (3a,b). The SEM technic provide information on crystallographic orientation. It also gives the geometry of vein filling at micrometric scales. The geometry of the vein filling at supported by the result of the fluid inclusion in the metamorphic quartz veins suggest a closed system behaviour. This closed system behavior, implies small scale transport of elements in a fluid by a diffusion process that may have taken place through the wall as a result of porosity. In other words, a chemical potential gradient due to pressure, temperature and stress is required to establish diffusion until filling of the crack. If the closed system becomes an open system by an abrupt opening on one side, a considerable decrease in pressure occurs, chemical condition changes and new reaction zones form. This is evidenced by the internal structure as seen under cross polars shown in Fig.3a,b. Fig 3a has a birefringence of 1st Order to 2nd Order for a thin section of 30μm thickness with undulose extinction. Two types of structure, similar to those described by Ramsey (1980), can be observed. First, a finely spaced banding is observed parallel to vein margins. The bands are separated by crystal of different sizes and varying birefringence. The geometry of the margins are thus preserved across the vein width, except when wall fragments have been included in the vein filling. Secondly, the simultaneous extinction of zones perpendicular to the banding defines the trails which link edge irregularities across the vein width. No inclusions or second phases are observed within these trails, so they are only extinction figures. The band width vary and the minimal width of one band is close to 1μm and the maximal is about 10 μm. Statistical analysis reveals a characteristic width of 5 μm and a random secession of band width (Renard et al., 2005). The quartz veins typically exhibit ribbon structures with conspicuous undulose extinction and some planar deformational features.

Table 1. Fluid data at Prestea mine, Prestea (ThTOT=Temperature of total homogenization).

<table>
<thead>
<tr>
<th>Inclusion Type</th>
<th>Fluid Composition</th>
<th>Salinity</th>
<th>ThTOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Monophase</td>
<td>H₂O</td>
<td>22-16 wt % NaCl</td>
<td>-</td>
</tr>
<tr>
<td>CO₂-H₂O</td>
<td>XH₂O : 0.73-0.9</td>
<td>XCO₂ : 0.082-0.255</td>
<td>XNaCl : 0.007-0.015</td>
</tr>
<tr>
<td>CO₂-rich Monophase</td>
<td>CO₂</td>
<td>1.74-0.847</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. Fluid data at Obuasi (CO₂= density of carbon dioxide, Bd= bulk density; XH₂O=mol fraction of water; XCO₂ = mol fraction of carbon dioxide; XNaCl=mol fraction of sodium chloride).

<table>
<thead>
<tr>
<th>Inclusion Type</th>
<th>Fluid Composition</th>
<th>Salinity</th>
<th>ThTOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Monophase</td>
<td>H₂O</td>
<td>10-25 wt % NaCl equivalent</td>
<td>-</td>
</tr>
<tr>
<td>CO₂-H₂O</td>
<td>XH₂O : 0.746-0.81</td>
<td>XCO₂ : 0.183-0.249</td>
<td>XNaCl : 0.005-0.007</td>
</tr>
<tr>
<td>CO₂-rich Monophase</td>
<td>CO₂d : 1.133-0.786</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The fluid inclusion microthermometric data indicated that there are two main types of fluids: partly aqueous (CO₂-H₂O); (CO₂-rich, liquid, monophase + biphase) and aqueous (H₂O-rich, monophase + biphase).

The limited range of the degree of fill (0.5 to 0.7) for the CO₂-rich and H₂O-rich inclusions indicates an original homogeneous fluid.

The auriferous fluid did not boil because neither the CO₂-rich nor H₂O-rich fluids homogenized upon heating into the liquid phase. The microthermometric data is presented graphically. All these graphical presentation, suggest that there are varying populations of inclusions and that there exist an intimate association between the quartz veins and the quartz veinlets.
Fig. 6. A scheme showing evolution of the Birimian auriferous fluid types

The CO₂-rich fluids homogenized at a higher temperature (350 - 400°C) than the H₂O-rich type (310 - 370°C). CO₂-rich fluid salinity ≈ 16 wt % NaCl equiv. Dominant trace gases in the fluid are CH₄ and N₂.

The significant amount of CH₄ + N₂ in CO₂ do not give a reasonable intersection value of the CO₂ and H₂O isochores for the determination of the true trapping temperature of the fluid. However, Oberthur et al. (1991) gave maximum temperatures of 400 to 500°C, based on pressure estimates from gaseous intrusions neglecting N₂. Manu (1991) used pressure corrections of 10-20°C from Potter (1977) to arrive at a minimum formation temperature of 370 - 410°C for the fluid whilst Schmidt et al. (1997) estimated 430°C based on P/T isochores for some category of CO₂-rich dominated inclusions for the fluid entrapment.

Fig. 7. Schematic illustration of different mineralization stages for gold formation in the Birimian environment in Ghana. (1), (2), (3), and (4) are different pockets of fracture zones that trapped the incoming auriferous fluid.

INTERPRETATION AND DISCUSSION

Formation of veins take three main steps: i) crack opening controlled by fluid pressure, stress or crystallization pressure, ii) transport of vein forming elements by diffusion and iii) the crystallization of the vein minerals.

Depending on the mechanism of formation and origin, banded quartz veins may differ in chemistry and mineral content. In the studied quartz banded vein, little or no chemical variations have been observed across the vein width. SEM images and field observations clearly show that a physical and morphological discontinuity exist between bands. The limits between successive bands are only marked by a discontinuity in the growth of minerals suggesting individual crack-seal emplacement, as proposed by the crack seal process of Ramsey (1980). Oscillations in fluid pressure and local stress are usually thought to open the interstice corresponding to each band (Ramsey, 1980). In the case of the quartz veins studied, two possible causes of cracking are proposed: Incremental stress release due to progressive unroofing of quartz blocks (Dilek et al.,...
1997) and accommodation of volume increases during the filling (O’Hanley, 1992).

The direction of orientation of the vein varies. Increase in size and direction, take place around preferred orientation (Fig 3b). This internal microstructure can only occur in a fluid filled open crack, where geometrical selection occurs during growth. The preservation of the wall geometry during vein formation is possible only if sealing of a crack is achieved before the opening of the following one. This is consistent with the model proposed by Hillgers et al. (2001).

According to the asymmetric geometry of the vein tip (Fig 3b) and SEM observations, it seems that cracking preferentially occurs at one vein wall interface and propagates. The shape of the vein margin is irregular and the morphology of the first crack is preserved during vein formation since each new crack follows the surface of the preceding one (Fig 2a,b and 3a,b). There is no evidence of margin dissolution of cataclastic deformation resulting from crack opening. This has been proposed by Davis et al. (1994) to be in favour of a slow and sub-critical propagation mode. Different mechanisms are considered to accommodate such a study state mode of propagation (Atkinson, 1984), but too few indices remain in the final deformation state to allow conclusions. Complete filling of the crack by precipitating hydrothermal quartz fluids allow stress transfer through the vein and the opening of another crack at the vein wall interface. Indeed, the different texture across the vein host rock interface makes this site a weak area (Hayford et al., 2009).

Given the very low solubility of quartz, transport of nutrients by advection through the fracture network would require huge amount of circulating fluid to fill each interstice totally with minerals (Fisher and Brantley, 1992). Other analysis conducted by Andreani (2003), confirm that the composition of the veins are product of the mineral composition of the adjacent wall rock. Therefore, the source nutrients may have been the immediate adjacent matrix. The result suggest a closed-system behavior implying small-scale transport of elements in a fluid by a diffusional process that may have taken place through the walls of the vein as a result of its porosity. A chemical potential gradient due to a pressure, temperature, stress or chemistry gradient is required to establish diffusion and need to be maintained until total filling of the crack. Supersaturation should also steadily occur in the interstice to allow mineral growth.

Examination of these points require the application of the macroscopic crystal growth theory. This theory commonly uses the capillary model based on the analogy between the liquid/vapour and crystal/solution system (Mullins and Sekerka, 1963). Crystal growth is only possible when it results in a decrease in Gibbs free energy G of the system. Therefore the variation in G may be written as follows:

\[ \Delta G = \Delta G_{\text{sol}} + \Delta G_{\text{surf}} < 0 \]

where:

\[ \Delta G_{\text{sol}} = n \Delta \mu, \]

is the volume free energy difference, with \( n \) the number of growth unit forming the crystal and having crossed the crystal/medium interface, and \( \Delta \mu \) the chemical potential difference undergone by one of these growth units. \( \Delta G_{\text{surf}} = + \gamma A \) is the crystal surface contribution to this Gibbs free energy change equal to the product of the crystal surface tension \( \gamma \) multiplied by the crystal surface area \( A \). Two different cases of nucleation are possible. These are homogeneous and heterogeneous nucleation. In nature, nucleation is predominantly heterogeneous because of the availability of preferential nucleation sites which lower the nucleation activation energy barrier. In this way, the convex nucleus decreases its area in contact with the solution lowering thereby the surface energy. This benefit is all the greater if the crystal and support is large. However, \( \Delta G_{\text{surf}} \) remains positive so that we should still have \( \Delta G_{\text{sol}} > 0 \) i.e. \( \Delta \mu = kT \ln \left( \frac{a}{a_{\text{eq}}} \right) > 0 \) for crystal growth, where \( k \) is Boltzman’s constant, \( T \) the absolute temperature, a the actual solute activity or solubility at \( T \). Accordingly, crystal growth is only possible if \( a/a_{\text{eq}} > 1 \) that is, if the solution is supersaturated.

Baronnet and Saul (2003) examined theoretically the conditions of crystallization in very tight interstices. They showed that tight interstitial opening favours crystallization in two ways: first, the simultaneous contact of the nucleus with both matrix walls decreases the surface energy for the supported nucleus, and secondly, good capillary wetting induces a concave crystal/solution meniscus. The second effect is important because it depresses the crystal solubility. An effect which is similar to a sub saturated pressure within a liquid in a case of capillary condensation. It is here to be noted that surface tension, while pulling the condensed phase, may now act to promote crystallization as \( \Delta G < 0 \) may be obeyed over a certain range of \( \Delta G_{\text{sol}} > 0 \) or for \( \Delta \mu > 0 \), i.e., for normally undersaturated solutions ( \( a/a_{\text{eq}} < 1 \)). The range of undersaturation involved, increases with the interstices and with the wetting capability of the crystals. This situation of crystal growth in under-saturated solutions may be seen as analogous, but opposite to that of Oswald ripening, where the capillary effect makes particles dissolution possible in a nominally supersaturated solution.

The driving force for diffusion of the quartz material from the wall to the crack, is related to the difference between the convex grain surface in the matrix and
the concave solid/solution meniscus in the interstice. Indeed, the Gibbs-Thomson relationship shows that the solubility of a crystal is inversely proportional to its size. The activity, therefore of the solute in the matrix will be enhanced by the small grain-size (normal capillary effect on solubility) and possibly also by the super solubility induced by stresses on matrix grains (Weyl, 1959). Contrasting with this, the equilibrium activity inside the vein interstice would be depressed by the above mentioned reversed solid/solution meniscus effect. The activity gradient responsible for solute diffusion from the matrix to the interstice could result from such physical contrast between the matrix, acting as the solute source, and the vein interstice acting as the sink. During progressive filling, such activity gradient and diffusional process would even increase due to progressive opening until complete filling. This process depends on the presence of an interstice and should thus stop when the crack is filled. However, its action might be resumed if the seeping capability of the wall for solute inflow were to be refreshed by successive cracks.

The proposed model of the fluid is consistent with the primary stage of a homogeneous fluid entrapment at different fracture zones followed by a significant drop in temperature due to cooling and increases in salinities at each site. The rise in salinity of H₂O-rich inclusions within a narrow temperature range signifies the unmixing of H₂O-rich from the parent fluid. Klemd (1998) used the characterization and similarities of several workers (e.g. Bowell, et al. 1990; Klemd et al. 1996 and Klemd and Hirdes, 1997) to suggest a single ore-process instead of a number of processes for the gold mineralization. For example, the deduced maximum temperature of 220 – 165 °C at 0.8 kbar of CO₂-bearing fluids, low salinities (< 5 wt % NaCl equiv.) on gold-bearing quartz veins at Obuasi mine was attributed to late stage mineralization by Bowell et al. (1990). This event modeled along this study would indicate that such an auriferous fluid was trapped at a lower crystal fracture zone as homogeneous entity and later cooled with resulting characteristics. Such phenomenon was likely to be envisaged for other fluids in different weak zones at different mining districts. On the basis of of this phenomenon, the estimation by Carranza et al. (2009) of about 40 undiscovered lode gold deposits in Southwestern Ghana looks realistic.

CONCLUSIONS
The evolutionary trends of banded gold bearing quartz veins suggest a crack seal type process of emplacement for the ore bearing fluid rich in CO₂ and H₂O. These fluids were originally homogeneous with dominant trace gases of CH₄ and N₂. Vein morphology and analysis favour diffusional transport of hydrothermal fluid from the adjacent matrix to the vein. Veins with discontinuities, create localized weak planes within massive gold bearing quartz veins that may preferentially accommodate further brittle deformation. This shows that under relatively low temperature condition, quartz can accommodate progressive deformation by a dissolution-diffusion crystallization process. Based on our observations we propose a model of formation for quartz banded veins that could explain:

i) the high departure from the equilibrium required for the precipitation of the crystals.

ii) the enhancement and the maintaining of a study state diffusional process for vein filling. This model takes advantage of capillary effect on crystallization that can occur in micrometer-size interstices. This study supports the view that, quartz microstructures may be able to record their environmental growth conditions. Thus they can act as a new tool for understanding crystal growth conditions under dynamic regimes. Further investigation are however needed, considering our inability to observe and collect data from other types of rocks in different geological settings.

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